Relativistic Corrections to Magnetic Properties

WERNER KUTZELNIGG

Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

Received 7 December 1998; accepted 22 February 1999

ABSTRACT: Relativistic corrections to magnetic properties (in principle to all orders in c^{-1}) are derived at a one-electron level. We start from the Dirac equation in a magnetic field and use direct perturbation theory (DPT). Thus, the singularities of methods based on the Foldy–Wouthuysen transformation are avoided. The nondegenerate case (where to zeroth order one must use a perturbation adapted nonrelativistic wave function) and the quasidegenerate case (which leads to effective Hamiltonians) are treated. The final results can be expressed on different levels: in terms of four-component spinors; in terms of two-component spinors representing the upper (large) and lower (small) components; and with complete elimination of the lower components, making use of the turnover rule that has to be understood in the distribution sense. Special attention is given to the magnetic susceptibilities and the NMR chemical shift. © 1999 John Wiley & Sons, Inc. J Comput Chem 20: 1199–1219, 1999

Keywords: NMR chemical shifts; magnetic susceptibilities; relativistic effects; direct perturbation theory; spin-orbit interaction

Introduction

Both the nonrelativistic limit of the eigenvalues of the Dirac equation and the leading relativistic corrections of $O(c^{-2})$, $O(c^{-4})$, etc., are most conveniently evaluated by means of *direct perturbation theory* (DPT),[1–4] which involves a change of the metric in four-component spinor space.[3] DPT is equivalent to perturbation theory based on an expansion of the reduced resolvent of the Dirac operator.[5] It is perfectly regular, which is at variance with perturbation theory based on the Foldy–Wouthysen (FW) transformed operator in which serious singularities beyond the leading order arise. The origin of these singularities has been analyzed and is well understood.[3,6–8]

Of course, DPT can also be applied in the context of double (or triple) perturbation theory in order to derive the relativistic corrections to properties. In this article we consider only magnetic properties like the magnetic dipole moment, the magnetic susceptibility, and NMR chemical shifts. The leading relativistic corrections were already derived starting from the FW transformed Hamil-

Correspondence to: W. Kutzelnigg; e-mail: Werner.Kutzelnigg@ruhr-uni-bochum.de

CCC 0192-8651 / 99 / 121199-21

tonian, concentrating mainly on spin-orbit coupling effects.[9–11] Such a derivation has various disadvantages. One is that spurious singularities arise beyond the leading orders, such that only the leading relativistic corrections can be treated. Even in the leading orders δ-function contributions must be introduced in an *ad hoc* way, which arise perfectly naturally if one uses DPT. Finally, DPT is more accurate, containing correction terms that vanish if the unperturbed problem is solved exactly but which are nonnegligible otherwise. In the FW-type approach one has (in order to justify certain expressions) to assume that the unperturbed problem has been solved exactly, which is usually not possible.

In this article we first consider single one-electron states. The formalism is then directly applicable to nondegenerate states; but it also works for states that are degenerate in the field-free nonrelativistic limit with the degeneracy removed by relativistic effects and a magnetic field, provided that one starts from perturbation adapted states in the sense of degenerate perturbation theory.

We start with a fully relativistic treatment, then treat the nonrelativistic limit in which the Lévy–Leblond equation plays a key role, and subsequently come to the leading relativistic corrections of $O(c^{-2})$ and the next relativistic corrections of $O(c^{-4})$. For all quantities of interest the equivalent expressions on various levels of a hierarchy are given. We start with expressions in terms of the perturbation expansion of modified (i.e., adjusted to the change of the metric) four-component spinors $\psi^{(2p,q)}$ (where $2p$ counts the order in c^{-1} and q that in powers of the field strength), which are very compact and are given in a form that is independent of the normalization condition. We then give expressions in terms of the upper and lower components $\varphi^{(2p,q)}$ and $\chi^{(2p,q)}$ of $\psi^{(2p,q)}$ and expressions where the lower (small) components are eliminated in favor of the upper (large) components $\varphi^{(2p,q)}$ only. At this level we specify the normalization. Here the need to apply the turnover rule arises, which has to be done in the distribution sense if singular operators are involved.[12] Thus, the Fermi contact term arises. At a fourth hierarchical level the matrix elements involving $\vec{\sigma}\vec{p}$ and $\vec{\sigma}\vec{A}$ operators are rearranged and decomposed into scalar and spin-dependent terms. This last level is only interesting in relation to a comparison with expressions in current use.[9–11,13,14] For a practical evaluation the first two levels are much more appropriate.

The problem of the regularization of upper and lower components has to be addressed. This will be done as a generalization of results known from the situation without a magnetic field.[15]

In the second part of this article we give a quasidegenerate formulation of the theory. Again we generalize a formalism recently presented for the case without an external magnetic field.[8,16]

For practical applications one must switch from the one-electron theory to a many-electron theory. The simplest of these is coupled Hartree–Fock theory, which will be presented in a forthcoming article.[17]

Single States of a One-Electron System

RELATIVISTIC ONE-ELECTRON SYSTEM IN A MAGNETIC FIELD

The relativistic theory of NMR chemical shifts was formulated long ago by Pyykkö[18,19] by generalizing the nonrelativistic theory of Ramsey.[20] Very recently a computer implementation on the full four-component spinor level in the context of relativistic Hartree–Fock was presented.[21] We give here a compact formulation for arbitrary magnetic fields as a starting point for the subsequent perturbation expansion.

Let the Dirac operator of a one-electron atom or molecule in the absence of a magnetic field be

$$D^{(0)} = \beta mc^2 + c\vec{\alpha}\vec{p} + V. \tag{1}$$

In the presence of a magnetic field $\vec{B}$ with vector potential $\vec{A}$ the Dirac operator becomes

$$D = D^{(0)} + c\lambda\vec{\alpha}\vec{A} = D^{(0)} + c\lambda\Omega, \tag{2}$$

$$\lambda = \begin{cases} -e/c = |e|/c & \text{in the Gaussian system of units,} \\ -e = |e| & \text{in the SI system.} \end{cases} \tag{3}$$

We will not specify the system of units for as long as possible. In the absence of a magnetic field it is very convenient to introduce atomic (Hartree) units. This is somewhat problematic in the presence of a magnetic field, because atomic units based on the Gaussian system or on the SI system are no longer identical. The only fundamental constant that directly appears in our Hamiltonian is the electron rest mass m. Hence, it will also arise in the perturbation expansion. Finally one will set $m = 1$ anyway, but it is advisable to keep m as

long as one has not specified the atomic units that one wants to use.

Expansion of the Dirac equation

$$D\psi_k = W_k \psi_k \tag{4}$$

in powers of λ leads to

$$D^{(0)}\psi_k^{(0)} = W_k^{(0)}\psi_k^{(0)}, \tag{5}$$

$$(D^{(0)} - W_k^{(0)})\psi_k^{(1)} + (c\Omega - W_k^{(1)})\psi_k^{(0)} = 0, \tag{6}$$

$$(D^{(0)} - W_k^{(0)})\psi_k^{(2)} + (c\Omega - W_k^{(1)})\psi_k^{(1)} - W_k^{(2)}\psi_k^{(0)} = 0, \ldots, \tag{7}$$

with

$$\psi_k = \psi_k^{(0)} + \lambda\psi_k^{(1)} + \cdots \tag{8}$$

$$W_k = W_k^{(0)} + \lambda W_k^{(1)} + \cdots \tag{9}$$

Scalar multiplying (5) to (7) from the left by $\psi_k^{(0)}$ we get

$$W_k^{(1)} = \langle \psi_k^{(0)}|c\Omega|\psi_k^{(0)}\rangle = \langle \varphi_k^{(0)}|c\vec{\sigma}\vec{A}|\chi_k^{(0)}\rangle + \langle \chi_k^{(0)}|c\vec{\sigma}\vec{A}|\varphi_k^{(0)}\rangle, \tag{10}$$

$$W_k^{(2)} = \langle \psi_k^{(0)}|c\Omega|\psi_k^{(1)}\rangle = \langle \varphi_k^{(0)}|c\vec{\sigma}\vec{A}|\chi_k^{(1)}\rangle + \langle \chi_k^{(0)}|c\vec{\sigma}\vec{A}|\varphi_k^{(1)}\rangle, \ldots, \tag{11}$$

where we decomposed $\psi_k^{(p)}$ into the upper (large) and lower (small) components, which are each two-component spinors,

$$\psi_k^{(p)} = \begin{pmatrix} \varphi_k^{(p)} \\ \chi_k^{(p)} \end{pmatrix}. \tag{12}$$

For the evaluation of $W_k^{(2)}$ we need $\psi_k^{(1)}$, which is obtained from (6). To make the solution unique, a normalization condition has to be imposed. Differences between different normalizations only arise to higher order. For both the ''unitary'' and the ''intermediate'' normalization we have

$$\langle \psi_k|\psi_k^{(0)}\rangle = \langle \psi_k^{(0)}|\psi_k^{(0)}\rangle = 1. \tag{13}$$

If there are two magnetic perturbations, Ω_1 and Ω_2, as in the context of the NMR chemical shifts or nuclear coupling constants, we have two equations of type (6)

$$(D^{(0)} - W_k^{(0)})\psi_k^{(1,0)} + (c\Omega_1 - W_k^{(1,0)})\psi_k^{(0)} = 0, \tag{14}$$

$$(D^{(0)} - W_k^{(0)})\psi_k^{(0,1)} + (c\Omega_2 - W_0^{(0,1)})\psi_k^{(0)} = 0, \tag{15}$$

and a ''mixed'' equation

$$(D^{(0)} - W_k^{(0)})\psi_k^{(1,1)} + (c\Omega_1 - W_k^{(1,0)})\psi_k^{(0,1)} + (c\Omega_2 - W_k^{(0,1)})\psi_k^{(1,0)} - W_k^{(1,1)}\psi_k^{(0)} = 0. \tag{16}$$

The result for $W_k^{(1,1)}$ is

$$\begin{aligned} W_k^{(1,1)} &= \langle \psi_k^{(0)}|c\Omega_1 - W_k^{(1,0)}|\psi_k^{(0,1)}\rangle \\ &\quad + \langle \psi_k^{(0)}|c\Omega_2 - W_k^{(0,1)}|\psi_k^{(1,0)}\rangle \\ &= -2\,\mathrm{Re}\langle \psi_k^{(1,0)}|D^{(0)} - W_k^{(0)}|\psi_k^{(0,1)}\rangle \\ &= 2\,\mathrm{Re}\langle \psi_k^{(0)}|c\Omega_1 - W_k^{(1,0)}|\psi_k^{(0,1)}\rangle \\ &= 2\,\mathrm{Re}\langle \psi_k^{(0)}|c\Omega_2 - W_k^{(0,1)}|\psi_k^{(1,0)}\rangle. \end{aligned} \tag{17}$$

The equivalence of the last two expressions is a manifestation of Dalgarno and Stewart's exchange theorem of double perturbation theory[22] that we encounter more often.

NONRELATIVISTIC LIMIT

Now we treat relativistic corrections as another perturbation: we deal with double perturbation theory for a single magnetic perturbation. This becomes straightforward if we limit our interest to electronic (rather than positronic) states and introduce a change in the metric[3] in the sense of DPT,

$$\psi_k \to \tilde{\psi}_k = \begin{pmatrix} \varphi_k \\ \tilde{\chi}_k \end{pmatrix} = \begin{pmatrix} \varphi_k \\ c\chi_k \end{pmatrix}, \tag{18}$$

such that the Dirac equation becomes

$$\tilde{D}\tilde{\psi} = E_k S\tilde{\psi}_k, \tag{19}$$

$$\tilde{D} = D_0 + c^{-2}D_2 + \lambda\Omega, \tag{20}$$

$$S = S_0 + c^{-2}S_2, \tag{21}$$

$$D_0 = \begin{pmatrix} V & \vec{\sigma}\vec{p} \\ \vec{\sigma}\vec{p} & -2m \end{pmatrix}; \quad D_2 = \begin{pmatrix} 0 & 0 \\ 0 & V \end{pmatrix}; \tag{22}$$

$$S_0 = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}; \quad S_2 = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}; \tag{23}$$

$$\Omega = \begin{pmatrix} 0 & \vec{\sigma}\vec{A} \\ \vec{\sigma}\vec{A} & 0 \end{pmatrix}; \quad E_k = W_k - mc^2. \tag{24}$$

We expand E_k and $\tilde{\psi}_k$ (or rather φ_k and $\tilde{\chi}_k$) in powers of c^{-1} and λ. To simplify the notation we omit the label k, which counts states, and we

consider just one state

$$\tilde{\psi}_k = \sum_{\mu,\nu} c^{-2\mu}\lambda^\nu \psi^{(2\mu,\nu)}, \tag{25}$$

$$\varphi_k = \sum_{\mu,\nu} c^{-2\mu}\lambda^\nu \varphi^{(2\mu,\nu)}, \tag{26}$$

$$\tilde{\chi}_k = \sum_{\mu,\nu} c^{-2\mu}\lambda^\nu \chi^{(2\mu,\nu)}, \tag{27}$$

$$E_k = \sum_{\mu,\nu} c^{-2\mu}\lambda^\nu E^{(2\mu,\nu)}. \tag{28}$$

Note that orders of c^{-1} are counted first and that only even orders of c^{-1} appear, the ''natural'' expansion parameter being actually c^{-2}. To simplify the notation we replace the superscript $(0,0)$ by (0). We choose $\psi^{(0)}$ as the limit for $\lambda \to 0$ and $c \to \infty$ of some perturbed states (i.e., as perturbation adapted). A generalization where this need not be assumed will be given in a later section. In the limit $c \to \infty$ the Dirac equation in a magnetic field reduces to the Lévy–Leblond equation in a magnetic field[12]

$$(D_0 + \lambda\Omega)\tilde{\psi} = ES_0\tilde{\psi}, \tag{29}$$

or in a component form

$$V\varphi + \vec{\sigma}\vec{p}\tilde{\chi} + \lambda\vec{\sigma}\vec{A}\tilde{\chi} = E\varphi, \tag{30}$$

$$\vec{\sigma}\vec{p}\varphi - 2m\tilde{\chi} + \lambda\vec{\sigma}\vec{A}\varphi = 0. \tag{31}$$

We expand further in powers of λ and get to zeroth-order the Lévy–Leblond equation[23] in the absence of a magnetic field:

$$D_0\psi^{(0)} = E_0^{(0)}S_0\psi^{(0)} \tag{32}$$

or

$$V\varphi^{(0)} + \vec{\sigma}\vec{p}\chi^{(0)} = E^{(0)}\varphi^{(0)}, \tag{33}$$

$$\vec{\sigma}\vec{p}\varphi^{(0)} - 2m\chi^{(0)} = 0. \tag{34}$$

Elimination of $\chi^{(0)}$ from (34) leads to

$$\chi^{(0)} = \frac{1}{2m}\vec{\sigma}\vec{p}\varphi^{(0)}, \tag{35}$$

$$H_0\varphi^{(0)} = E^{(0)}\varphi^{(0)}; \quad H_0 = V + \frac{1}{2m}\vec{p}^{\,2}. \tag{36}$$

Expansion of the Lévy–Leblond equation in powers of λ leads further to

$$(D_0 - E^{(0)}S_0)\psi^{(0,1)} + (\Omega - E^{(0,1)}S_0)\psi^{(0)} = 0; \tag{37}$$

$$(D_0 - E^{(0)}S_0)\psi^{(0,2)} + (\Omega - E^{(0,1)}S_0)\psi^{(0,1)} - E^{(0,2)}S_0\psi^{(0)} = 0, \ldots, \tag{38}$$

or in component form

$$(V - E^{(0)})\varphi^{(0,1)} + \vec{\sigma}\vec{p}\chi^{(0,1)} + \vec{\sigma}\vec{A}\chi^{(0)} - E^{(0,1)}\varphi^{(0)} = 0, \tag{39}$$

$$\vec{\sigma}\vec{p}\varphi^{(0,1)} - 2m\chi^{(0,1)} + \vec{\sigma}\vec{A}\varphi^{(0)} = 0, \tag{40}$$

$$(V - E^{(0)})\varphi^{(0,2)} + \vec{\sigma}\vec{p}\chi^{(0,2)} + \vec{\sigma}\vec{A}\chi^{(0,1)} - E^{(0,1)}\varphi^{(0,1)} - E^{(0,2)}\varphi^{(0)} = 0, \tag{41}$$

$$\vec{\sigma}\vec{p}\varphi^{(0,2)} - 2m\chi^{(0,2)} + \vec{\sigma}\vec{A}\varphi^{(0,1)} = 0. \tag{42}$$

From these equations we get

$$\chi^{(0,1)} = \frac{1}{2m}\left\{\vec{\sigma}\vec{p}\varphi^{(0,1)} + \vec{\sigma}\vec{A}\varphi^{(0)}\right\}, \tag{43}$$

$$(H_0 - E^{(0)})\varphi^{(0,1)} + \left\{\frac{1}{2m}\left[\vec{\sigma}\vec{p}, \vec{\sigma}\vec{A}\right]_+ - E^{(0,1)}\right\}\varphi^{(0)} = 0, \tag{44}$$

$$\chi^{(0,2)} = \frac{1}{2m}\left\{\vec{\sigma}\vec{p}\varphi^{(0,2)} + \vec{\sigma}\vec{A}\varphi^{(0,1)}\right\}, \tag{45}$$

$$(H_0 - E^{(0)})\varphi^{(0,2)} + \left\{\frac{1}{2m}\left[\vec{\sigma}\vec{p}, \vec{\sigma}\vec{A}\right]_+ - E^{(0,1)}\right\}\varphi^{(0,1)} + \left\{\frac{1}{2m}\vec{A}^2 - E^{(0,2)}\right\}\varphi^{(0)} = 0. \tag{46}$$

Choosing the *intermediate normalization for the large component*,

$$\langle\psi^{(0)}|S_0|\psi^{(0)}\rangle = \langle\varphi^{(0)}|\varphi^{(0)}\rangle = 1, \tag{47}$$

$$\langle\psi^{(0)}|S_0|\psi^{(0,k)}\rangle = \langle\varphi^{(0)}|\varphi^{(0,k)}\rangle = 0 \quad k \geq 1, \tag{48}$$

we get for the first-order energy

$$\begin{aligned} E^{(0,1)} &= \langle\psi^{(0)}|\Omega|\psi^{(0)}\rangle \\ &= \langle\varphi^{(0)}|\vec{\sigma}\vec{A}|\chi^{(0)}\rangle + \langle\chi^{(0)}|\vec{\sigma}\vec{A}|\varphi^{(0)}\rangle, \\ &= \frac{1}{2m}\langle\varphi^{(0)}|(\vec{\sigma}\vec{A})(\vec{\sigma}\vec{p})|\varphi^{(0)}\rangle \\ &\quad + \frac{1}{2m}\langle\vec{\sigma}\vec{p}\varphi^{(0)}|\vec{\sigma}\vec{A}\varphi^{(0)}\rangle. \end{aligned} \tag{49}$$

For the second-order energy we obtain

$$\begin{aligned} E^{(0,2)} &= \langle \psi^{(0)}|\Omega - E^{(0,1)}S_0|\psi^{(0,1)}\rangle \\ &= \langle \varphi^{(0)}|\vec{\sigma}\vec{A}|\chi^{(0,1)}\rangle + \langle \chi^{(0)}|\vec{\sigma}\vec{A}|\varphi^{(0,1)}\rangle \\ &= \frac{1}{2m}\langle \varphi^{(0)}|(\vec{\sigma}\vec{A})^2|\varphi^{(0)}\rangle \\ &\quad + \frac{1}{2m}\langle \varphi^{(0)}|(\vec{\sigma}\vec{A})(\vec{\sigma}\vec{p})|\varphi^{(0,1)}\rangle \\ &\quad + \frac{1}{2m}\langle \vec{\sigma}\vec{p}\varphi^{(0)}|\vec{\sigma}\vec{A}|\varphi^{(0,1)}\rangle. \end{aligned} \tag{50}$$

This expression is valid if $\psi^{(0,1)}$ has been obtained as that particular solution of (44) that satisfies the normalization condition (48). Higher orders in λ are straightforward. Further simplification of $E^{(0,1)}$ and $E^{(0,2)}$ is possible if $\vec{A}$ satisfies the Coulomb gauge and has no singularities, such that the turnover rule can be applied safely:

$$\begin{aligned} E^{(0,1)} &= \frac{1}{2m}\langle \varphi^{(0)}|[\vec{\sigma}\vec{A}, \vec{\sigma}\vec{p}]_+|\varphi^{(0)}\rangle \\ &= \frac{1}{2m}\langle \varphi^{(0)}|\vec{A}\vec{p} + \vec{p}\vec{A} + i\vec{\sigma}\vec{A}\times\vec{p} \\ &\quad + i\vec{\sigma}\vec{p}\times\vec{A}|\varphi^{(0)}\rangle \\ &= \frac{1}{m}\langle \varphi^{(0)}|\vec{A}\vec{p}|\varphi^{(0)}\rangle + \frac{\hbar}{2m}\langle \varphi^{(0)}|\vec{\sigma}\cdot\vec{B}|\varphi^{(0)}\rangle, \end{aligned} \tag{51}$$

where we used

$$\text{div}\ \vec{A} = 0; \quad \vec{B} = \text{curl}\ \vec{A}, \tag{52}$$

$$\begin{aligned} E^{(0,2)} &= \frac{1}{2m}\langle \varphi^{(0)}|A^2|\varphi^{(0)}\rangle \\ &\quad + \frac{1}{2m}\langle \varphi^{(0)}|[\vec{\sigma}\vec{A}, \vec{\sigma}\vec{p}]_+|\varphi^{(0,1)}\rangle \\ &= \frac{1}{2m}\langle \varphi^{(0)}|A^2|\varphi^{(0)}\rangle + \frac{1}{m}\langle \varphi^{(0)}|\vec{A}\vec{p}|\varphi^{(0,1)}\rangle \\ &\quad + \frac{\hbar}{2m}\langle \varphi^{(0)}|\vec{\sigma}\cdot\vec{B}|\varphi^{(0,1)}\rangle. \end{aligned} \tag{53}$$

For the same situation the inhomogeneous differential equation (44) for $\varphi^{(0,1)}$ becomes

$$(H_0 - E^{(0)})\varphi^{(0,1)} + \left(\frac{1}{m}\vec{A}\vec{p} + \frac{\hbar}{2m}\vec{\sigma}\cdot\vec{B}\right)\varphi^{(0)} - E^{(0,1)}\varphi^{(0)} = 0. \tag{54}$$

For a homogeneous field with

$$\vec{A} = \frac{1}{2}\vec{B}\times(\vec{r} - \vec{R}), \tag{55}$$

a further simplification is possible noting that

$$\vec{A}\cdot\vec{p} = \frac{1}{2}B\cdot\{(\vec{r} - \vec{R})\times\vec{p}\} = \frac{1}{2}\vec{B}\cdot\vec{l}, \tag{56}$$

where $\vec{l}$ is the angular momentum with respect to the origin $\vec{R}$, and that

$$\vec{s} = \frac{\hbar}{2}\vec{\sigma} \tag{57}$$

is the spin operator such that

$$E^{(0,1)} = \frac{1}{2m}\langle \varphi^{(0)}|\vec{B}\cdot(\vec{l} + 2\vec{s})|\varphi^{(0)}\rangle, \tag{58}$$

$$\begin{aligned} E^{(0,2)} &= \frac{1}{2m}\langle \varphi^{(0)}|A^2|\varphi^{(0)}\rangle \\ &\quad + \frac{1}{2m}\langle \varphi^{(0)}|\vec{B}\cdot(\vec{l} + 2\vec{s})|\varphi^{(0,1)}\rangle. \end{aligned} \tag{59}$$

As an alternative to the intermediate normalization of (47) and (48), we can choose the unitary normalization, which in the nonrelativistic limit implies

$$\langle \varphi^{(0)}|\varphi^{(0)}\rangle = 1; \quad \langle \varphi^{(0)}|\varphi^{(0,1)}\rangle = 0; \tag{60}$$

$$2\,\text{Re}\langle \varphi^{(0)}|\varphi^{(0,2)}\rangle + \langle \varphi^{(0,1)}|\varphi^{(0,1)}\rangle = 0\ldots. \tag{61}$$

With this normalization there is no change for $E^{(0,1)}$ nor for $E^{(0,2)}$, but starting with $E^{(0,3)}$ there are formal differences, although the $E^{(0,k)}$ are, of course (at variance with the $\psi^{(0,k)}$), independent of the normalization.

The results for $E^{(0,1)}$ and $E^{(0,2)}$ are the same that one gets in nonrelativistic theory starting from the Hamiltonian with an *ad hoc* spin term

$$H = \frac{1}{2m}(\vec{p} + \lambda\vec{A})^2 + V + \frac{1}{m}\vec{B}\cdot\vec{s}. \tag{62}$$

Note that for a homogenous external magnetic field $\vec{B}$, spin does not contribute to $\varphi^{(0,1)}$.

For a vector potential that is singular at the position of a nucleus, like that generated by the nuclear spin, the situation is more complicated, because the turnover rule cannot be used in the naive sense and the theory of distributions must be applied. For $E^{(0,1)}$ one is so led to the Fermi contact interaction that was previously derived[12] from the Lévy–Leblond equation[23] in a straightforward way. The turnover rule is based on an

integration by parts, assuming that the ''boundary term'' vanishes. This is no longer justified for an integral that is singular at the position of a nucleus. To formally save the turnover rule for the vector potential

$$\vec{A} = \frac{\vec{\mu} \times \vec{r}}{r^3} \tag{63}$$

of a point nucleus at $\vec{r} = 0$, relation (52) has to be replaced by[12]

$$\text{curl } \vec{A} = \vec{B}_f + \vec{b}^{(0)} + \vec{b}^{(2)}, \tag{64}$$

where $\vec{B}_f$ is the curl of $\vec{A}$ in the function sense and $\vec{b}^{(0)}$ and $\vec{b}^{(2)}$ are additional contributions in the distribution sense:

$$\vec{B}_f = -\frac{\vec{\mu}}{r^3} + \frac{3(\vec{\mu}\vec{r})\vec{r}}{r^5}, \tag{65}$$

$$\vec{b}^{(0)} = \frac{2}{3}\frac{\vec{\mu}}{r^2}\delta(r), \tag{66}$$

$$\vec{b}^{(2)} = \frac{1}{3}\frac{\vec{\mu}}{r^2}\delta(r) - \vec{r}\frac{\vec{\mu}\vec{r}}{r^4}\delta(r). \tag{67}$$

The term $\vec{\sigma}\vec{b}^{(0)}$ is spherically symmetric and is called the Fermi contact term.

If we have two magnetic perturbation characterized by $\vec{A}_1$ and $\vec{A}_2$, we have equations like (37) and (38) or (39)–(42) for either perturbation and *mixed* equations such as

$$\begin{aligned}(D_0 - E^{(0)}S_0)\psi^{(0,1,1)} + (\Omega_1 - E^{(0,1,0)}S_0)\psi^{(0,0,1)} \\ + (\Omega_2 - E^{(0,0,1)}S_0)\psi^{(0,1,0)} \\ - E^{(0,1,1)}S_0\psi^{(0)} = 0,\end{aligned} \tag{68}$$

from which we get

$$\begin{aligned}E^{(0,1,1)} = \langle \psi^{(0)}|\Omega_1 - E^{(0,1,0)}S_0|\psi^{(0,0,1)}\rangle \\ + \langle \psi^{(0)}|\Omega_2 - E^{(0,0,1)}S_0|\psi^{(0,1,0)}\rangle.\end{aligned} \tag{69}$$

By means of (37) and (38) this can be reformulated to

$$\begin{aligned}E^{(0,1,1)} &= -2\,\text{Re}\langle \psi^{(0,1,0)}|D_0 - E^{(0)}S_0|\psi^{(0,0,1)}\rangle \\ &= 2\,\text{Re}\langle \psi^{(0)}|\Omega_1 - E^{(0,1,0)}S_0|\psi^{(0,0,1)}\rangle \\ &= 2\,\text{Re}\langle \psi^{(0)}|\Omega_2 - E^{(0,0,1)}S_0|\psi^{(0,1,0)}\rangle.\end{aligned} \tag{70}$$

The two equivalent expressions involving either $\psi^{(0,0,1)}$ (due to the second perturbation) or $\psi^{(0,1,0)}$ (due to the first perturbation) are again a manifestation of Dalgarno and Stewart's exchange theorem of double perturbation theory.[22]

We can rewrite $E^{(0,1,1)}$ as (for either normalization)

$$\begin{aligned}E^{(0,1,1)} &= 2\,\text{Re}\Big\{\langle \varphi^{(0)}|\vec{\sigma}\vec{A}_2|\chi^{(0,1,0)}\rangle \\ &\quad + \langle \chi^{(0)}|\vec{\sigma}\vec{A}_2|\varphi^{(0,1,0)}\rangle\Big\} \\ &= \frac{1}{m}\Big\{\text{Re}\langle \varphi^{(0)}\Big|\Big(\vec{\sigma}\vec{A}_2\Big)\Big(\vec{\sigma}\vec{A}_1\Big)\Big|\varphi^{(0)}\rangle \\ &\quad + \langle \varphi^{(0)}\Big|\Big(\vec{\sigma}\vec{A}_2\Big)\Big(\vec{\sigma}\vec{p}\Big)\Big|\varphi^{(0,1,0)}\rangle \\ &\quad + \langle \vec{\sigma}\vec{p}\varphi^{(0)}|\vec{\sigma}\vec{A}_2|\varphi^{(0,1,0)}\rangle\Big\}\end{aligned} \tag{71}$$

or with A_1 and A_2 exchanged.

If one of the magnetic fields is singular, as that due to the nuclear magnetic moment in the case of the NMR chemical shift, it is advisable to choose the singular field as $\vec{A}_2$, because then $\varphi^{(0,1,0)}$ is regular and singularities arise only in the operators, which can be dealt with by applying the turnover rule in the distribution sense.

Hence, we can apply the turnover rule, provided that curl $\vec{A}_2$ is understood in the sense of (64):

$$\begin{aligned}E^{(0,1,1)} = \frac{1}{m}\text{Re}\Big\{\langle \varphi^{(0)}|\vec{A}_1 \cdot \vec{A}_2|\varphi^{(0)}\rangle \\ + \langle \varphi^{(0)}|2\vec{A}_2 \cdot \vec{p} + \hbar\vec{\sigma}\cdot\text{curl } \vec{A}_2|\varphi^{(0,1,0)}\rangle\Big\}.\end{aligned} \tag{72}$$

This is (for $\vec{A}_1$ due to a homogeneous field) the classical nonrelativistic expression of the NMR chemical shift, plus an additional Fermi contact like spin-dependent contribution. If one averages over spin, the last term vanishes, of course.

If $\vec{A}_1$ and $\vec{A}_2$ are both singular, even more care is necessary. In fact, then the perturbation series no longer exists but the lower orders are well-defined nevertheless. If one wants to go to higher orders one must explicitly stipulate that the nucleus has a finite extension and cannot be regarded as a magnetic point dipole. To the leading order the approximation of the nucleus as a point dipole is well justified[12], however.

LEADING RELATIVISTIC CORRECTIONS

To get the leading relativistic corrections we need, in addition to (32), (37), and (38), the following equations derived from expanding the Dirac

equation in powers of c^{-2} and λ:

$$(D_0 - E^{(0)}S_0)\psi^{(2,0)} + (D_2 - E^{(0)}S_2 - E^{(2,0)}S_0)\psi^{(0)} = 0, \quad (73)$$

$$(D_0 - E^{(0)}S_0)\psi^{(2,1)} + (D_2 - E^{(0)}S_2 - E^{(2,0)}S_0)\psi^{(0,1)} + (\Omega - E^{(0,1)}S_0)\psi^{(2,0)} - (E^{(2,1)}S_0 + E^{(0,1)}S_2)\psi^{(0)} = 0, \quad (74)$$

$$(D_0 - E^{(0)}S_0)\psi^{(2,2)} + (D_2 - E^{(0)}S_2 - E^{(2,0)}S_0)\psi^{(0,2)} + (\Omega - E^{(0,1)}S_0)\psi^{(2,1)} - E^{(0,2)}S_0\psi^{(2,0)} - (E^{(2,1)}S_0 + E^{(0,1)}S_2)\psi^{(0,1)} - (E^{(2,2)}S_0 + E^{(0,2)}S_2)\psi^{(0)} = 0. \quad (75)$$

In component form (73) and (74) become

$$(V - E^{(0)})\varphi^{(2,0)} + \vec{\sigma}\vec{p}\chi^{(2,0)} - E^{(2,0)}\varphi^{(0)} = 0, \quad (76)$$

$$\vec{\sigma}\vec{p}\varphi^{(2,0)} - 2m\chi^{(2,0)} + (V - E^{(0)})\chi^{(0)} = 0, \quad (77)$$

$$(V - E^{(0)})\varphi^{(2,1)} + \vec{\sigma}\vec{p}\chi^{(2,1)} - E^{(2,0)}\varphi^{(0,1)} + \vec{\sigma}\vec{A}\chi^{(2,0)} - E^{(0,1)}\varphi^{(2,0)} - E^{(2,1)}\varphi^{(0)} = 0, \quad (78)$$

$$\vec{\sigma}\vec{p}\varphi^{(2,1)} - 2m\chi^{(2,1)} + (V - E^{(0)})\chi^{(0,1)} + \vec{\sigma}\vec{A}\varphi^{(2,0)} - E^{(0,1)}\chi^{(0)} = 0, \quad (79)$$

from which we get

$$\chi^{(2,0)} = \frac{1}{2m}\left\{\vec{\sigma}\vec{p}\varphi^{(2,0)} + (V - E^{(0)})\chi^{(0)}\right\}, \quad (80)$$

$$(H_0 - E^{(0)})\varphi^{(2,0)} + \left\{\frac{1}{4m^2}\vec{\sigma}\vec{p}(V - E^{(0)})\vec{\sigma}\vec{p} - E^{(2,0)}\right\}\varphi^{(0)} = 0, \quad (81)$$

$$\chi^{(2,1)} = \frac{1}{2m}\left\{\vec{\sigma}\vec{p}\varphi^{(2,1)} + (V - E^{(0)})\chi^{(0,1)} + \vec{\sigma}\vec{A}\varphi^{(2,0)} - E^{(0,1)}\chi^{(0)}\right\}, \quad (82)$$

$$(H_0 - E^{(0)})\varphi^{(2,1)} + \left\{\frac{1}{4m^2}\vec{\sigma}\vec{p}(V - E^{(0)})\vec{\sigma}\vec{p} - E^{(2,0)}\right\}\varphi^{(0,1)} + \left\{\frac{1}{2m}\left[\vec{\sigma}\vec{p}, \vec{\sigma}\vec{A}\right]_+ - E^{(0,1)}\right\}\varphi^{(2,0)} + \left\{\frac{1}{4m^2}\left[\vec{\sigma}\vec{p}(V - E^{(0)})\vec{\sigma}\vec{A} + \vec{\sigma}\vec{A}(V - E^{(0)})\vec{\sigma}\vec{p}\right] - E^{(2,1)} - \frac{1}{2m}E^{(0,1)}T\right\}\varphi^{(0)} = 0. \quad (83)$$

From (73) one obtains the well-known result[3]

$$E^{(2,0)} = \langle\psi^{(0)}|D_2 - E^{(0)}S_2|\psi^{(0)}\rangle = \langle\chi^{(0)}|V - E^{(0)}|\chi^{(0)}\rangle, \quad (84)$$

which is independent of the normalization condition. This can be rewritten as

$$E^{(2,0)} = \frac{1}{4m^2}\langle\varphi^{(0)}|\vec{\sigma}\vec{p}(H_0 - E^{(0)} - T)\vec{\sigma}\vec{p}|\varphi^{(0)}\rangle = \frac{1}{4m^2}\langle\varphi^{(0)}|\vec{\sigma}\vec{p}\left[H_0, \vec{\sigma}\vec{p}\right]|\varphi^{(0)}\rangle + \frac{1}{2m}\langle\varphi^{(0)}|T(H_0 - E^{(0)})|\varphi^{(0)}\rangle - \frac{1}{2m}\langle\varphi^{(0)}|T^2|\varphi^{(0)}\rangle. \quad (85)$$

The first term in the last expression contains the Darwin and the spin-orbit term; the second one is a correction term[15,24,25] that vanishes if $\varphi^{(0)}$ is an eigenfunction of H_0, but is important otherwise; and the third term is known as the velocity mass term. The first term in the last expression of (85) can be further reformulated to

$$\frac{1}{4m^2}\langle\varphi^{(0)}|\vec{\sigma}\vec{p}\left[V, \vec{\sigma}\vec{p}\right]|\varphi^{(0)}\rangle = -\frac{1}{8m^2}\langle\varphi^{(0)}|\left[\vec{\sigma}\vec{p}, \left[\vec{\sigma}\vec{p}, V\right]\right]|\varphi^{(0)}\rangle = \frac{\hbar^2}{8m^2}\langle\varphi^{(0)}|\nabla^2 V|\varphi^{(0)}\rangle + \frac{\hbar}{4m^2}\langle\varphi^{(0)}|\vec{\sigma}\cdot(\nabla V \times \vec{p})|\varphi^{(0)}\rangle, \quad (86)$$

such that one recognizes the Darwin and spin-orbit terms explicitly. The latter is the only spin-dependent contribution to $E^{(2,0)}$.

We get from (74) for the first-order relativistic correction to a first-order magnetic property

$$E^{(2,1)} = \langle\psi^{(0)}|D_2 - E^{(0)}S_2 - E^{(2,0)}S_0|\psi^{(0,1)}\rangle + \langle\psi^{(0)}|\Omega - E^{(0,1)}S_0|\psi^{(2,0)}\rangle - E^{(0,1)}\langle\psi^{(0)}|S_2|\psi^{(0)}\rangle. \quad (87)$$

Reformulation in the sense of the Dalgarno exchange theorem of double perturbation theory is

possible:

$$\begin{aligned} E^{(2,1)} &= -\langle \psi^{(2,0)}| D_0 - E^{(0)} S_0 |\psi^{(0,1)}\rangle \\ &\quad + \langle \psi^{(0)}| \Omega - E^{(0,1)} S_0 |\psi^{(2,0)}\rangle \\ &\quad - E^{(0,1)} \langle \psi^{(0)}| S_2 |\psi^{(0)}\rangle \\ &= 2\,\mathrm{Re}\langle \psi^{(2,0)}| \Omega - E_0^{(0,1)} S_0 |\psi^{(0)}\rangle \\ &\quad - E^{(0,1)} \langle \psi^{(0)}| S_2 |\psi^{(0)}\rangle \\ &= 2\,\mathrm{Re}\Big\{ \langle \varphi^{(2,0)}| \vec{\sigma}\vec{A}| \chi^{(0)}\rangle + \langle \chi^{(2,0)}| \vec{\sigma}\vec{A}| \varphi^{(0)}\rangle \Big\} \\ &\quad - E^{(0,1)} \langle \chi^{(0)}| \chi^{(0)}\rangle; \end{aligned} \tag{88}$$

alternatively,

$$\begin{aligned} E^{(2,1)} &= \langle \psi^{(0)}| D_2 - E^{(0)} S_2 - E^{(2,0)} S_0 |\psi^{(0,1)}\rangle \\ &\quad - \langle \psi^{(0,1)}| D_0 - E^{(0)} S_0 |\psi^{(2,0)}\rangle \\ &\quad - E^{(0,1)} \langle \psi^{(0)}| S_2 |\psi^{(0)}\rangle \\ &= 2\,\mathrm{Re}\langle \psi^{(0)}| D_2 - E^{(0)} S_2 - E^{(2,0)} S_0 |\psi^{(0,1)}\rangle \\ &\quad - E^{(0,1)} \langle \psi^{(0)}| S_2 |\psi^{(0)}\rangle \\ &= 2\,\mathrm{Re}\langle \chi^{(0)}| V - E^{(0)} |\chi^{(0,1)}\rangle \\ &\quad - E^{(0,1)} \langle \chi^{(0)}| \chi^{(0)}\rangle. \end{aligned} \tag{89}$$

In the last lines of (88) and (89) we used the intermediate normalization for the large component, which implies in addition to (47) and (48) that

$$\langle \varphi^{(0)}| \varphi^{(q,0)}\rangle = 0 \quad q > 0. \tag{90}$$

In the unitary normalization we have in addition to (60) and (61),

$$2\,\mathrm{Re}\langle \varphi^{(0)}| \varphi^{(2,0)}\rangle + \langle \chi^{(0)}| \chi^{(0)}\rangle = 0, \tag{91}$$

$$2\,\mathrm{Re}\langle \varphi^{(0)}| \varphi^{(4,0)}\rangle + \langle \varphi^{(2,0)}| \varphi^{(2,0)}\rangle + 2\,\mathrm{Re}\langle \chi^{(0)}| \chi^{(2,0)}\rangle = 0. \tag{92}$$

Hence, in unitary normalization the last expression in (88) is changed to

$$E^{(2,1)} = 2\,\mathrm{Re}\Big\{ \langle \varphi^{(2,0)}| \vec{\sigma}\vec{A}| \chi^{(0)}\rangle + \langle \chi^{(2,0)}| \vec{\sigma}\vec{A}| \varphi^{(0)}\rangle \Big\} \tag{93}$$

while (89) is unchanged. In (88) $E^{(2,1)}$ appears as a relativistic correction to the expectation value of $[\vec{\sigma}\vec{A}, \vec{\sigma}\vec{p}]_+$ (i.e, the magnetic moment), including the Fermi contact term, while (89) is a correction of the leading relativistic energy due to the magnetic field.

Still further reformulation is possible in either case if one uses (35), (43), and (80). Even more simplifications are possible if the turnover rule can be applied safely.

Then we get

$$\begin{aligned} E^{(2,1)} &= \frac{1}{m}\mathrm{Re}\Big\{ \langle \varphi^{(2,0)}| (\vec{\sigma}\vec{A})\big(\vec{\sigma}\vec{p}\big)| \varphi^{(0)}\rangle \\ &\quad + \langle \varphi^{(2,0)}| \big(\vec{\sigma}\vec{p}\big)(\vec{\sigma}\vec{A})| \varphi^{(0)}\rangle \\ &\quad + \langle \chi^{(0)}| (V - E^{(0)})\vec{\sigma}\vec{A}| \varphi^{(0)}\rangle \Big\} \\ &\quad - \frac{1}{2m} E^{(0,1)} \langle \varphi^{(0)}| T| \varphi^{(0)}\rangle \\ &= \frac{1}{m}\mathrm{Re}\langle \varphi^{(2,0)}| [\vec{\sigma}\vec{A}, \vec{\sigma}\vec{p}]_+ | \varphi^{(0)}\rangle \\ &\quad + \frac{1}{2m^2}\mathrm{Re}\langle \varphi^{(0)}| \vec{\sigma}\vec{p}(V - E^{(0)})\vec{\sigma}\vec{A}| \varphi^{(0)}\rangle \\ &\quad - \frac{1}{2m} E^{(0,1)} \langle \varphi^{(0)}| T| \varphi^{(0)}\rangle \end{aligned} \tag{94}$$

or

$$\begin{aligned} E^{(2,1)} &= \frac{1}{2m^2}\mathrm{Re}\Big\{ \langle \varphi^{(0)}| \vec{\sigma}\vec{p}(V - E^{(0)})\vec{\sigma}\vec{A}| \varphi^{(0)}\rangle \\ &\quad + \langle \varphi^{(0)}| \vec{\sigma}\vec{p}(V - E^{(0)})\vec{\sigma}\vec{p}| \varphi^{(0,1)}\rangle \Big\} \\ &\quad - \frac{1}{2m} E^{(0,1)} \langle \varphi^{(0)}| T| \varphi^{(0)}\rangle. \end{aligned} \tag{95}$$

While (95) holds in either normalization, in (94) the last term must be omitted if the unitary normalization is used. Further reformulation of the expressions involving $[(\vec{\sigma}\vec{A}), (\vec{\sigma}\vec{p})]_+$ or $\vec{\sigma}\vec{p}(V - E^{(0)})\vec{\sigma}\vec{p}$ is possible on the same lines as outlined previously.

In fact, the term involving $[\vec{\sigma}\vec{A}, \vec{\sigma}\vec{p}]_+$ can be replaced by

$$[\vec{\sigma}\vec{A}, \vec{\sigma}\vec{p}]_+ = \begin{cases} \vec{B}\cdot\big(\vec{l} + 2\vec{s}\big) \\ \qquad \text{for a homogeneous field,} \\ 2\vec{A}\cdot\vec{p} + \hbar\vec{\sigma}\cdot\mathrm{curl}\ \vec{A} \\ \qquad \text{for the field of a nucleus,} \end{cases} \tag{96}$$

with curl $\vec{A}$ in the distribution sense as indicated in (64). The term involving twice $\vec{\sigma}\vec{p}$ can be reformulated as in (85) and (86) into Darwin, velocity mass, and spin-orbit terms, plus a correction term, which vanishes if $(H_0 - E^{(0)})\varphi^{(0)} = 0$. The mixed term present in (94) and (95) can be reformulated

as [provided that $(H_0 - E^{(0)})\varphi^{(0)} = 0$]

$$\frac{1}{2m^2}\mathrm{Re}\langle \varphi^{(0)}|\vec{\sigma}\vec{p}(V - E^{(0)})\vec{\sigma}\vec{A}|\varphi^{(0)}\rangle$$
$$= \frac{1}{2m^2}\mathrm{Re}\Big\{\langle \varphi^{(0)}|\vec{\sigma}\vec{p}(H_0 - E^{(0)})\vec{\sigma}\vec{A}|\varphi^{(0)}\rangle - \langle \varphi^{(0)}|T\big(\vec{\sigma}\vec{p}\big)(\vec{\sigma}\vec{A})|\varphi^{(0)}\rangle\Big\}$$
$$= \frac{1}{2m^2}\mathrm{Re}\Big\{\langle \varphi^{(0)}|\Big[\vec{\sigma}\vec{p}, V\Big]\vec{\sigma}\vec{A}|\varphi^{(0)}\rangle - \langle \varphi^{(0)}|T\big(\vec{\sigma}\vec{p}\big)(\vec{\sigma}\vec{A})|\varphi^{(0)}\rangle\Big\}. \quad (97)$$

Both contributions give rise to scalar terms and spin-dependent terms.

The leading relativistic correction to a second-order magnetic property is a little more complicated. From (75) we get

$$E^{(2,2)} = \langle \psi^{(0)}|D_2 - E^{(0)}S_2 - E^{(2,0)}S_0|\psi^{(0,2)}\rangle + \langle \psi^{(0)}|\Omega - E^{(0,1)}S_0|\psi^{(2,1)}\rangle - E^{(0,2)}\langle \psi^{(0)}|S_0|\psi^{(2,0)}\rangle - E^{(0,1)}\langle \psi^{(0)}|S_2|\psi^{(0,1)}\rangle - E^{(0,2)}\langle \psi^{(0)}|S_2|\psi^{(0)}\rangle - E^{(2,1)}\langle \psi^{(0)}|S_0|\psi^{(0,1)}\rangle. \quad (98)$$

One wants to eliminate $\psi^{(0,2)}$ and $\psi^{(2,1)}$ to arrive at

$$E^{(2,2)} = -\langle \psi^{(2,0)}|D_0 - E^{(0)}S_0|\psi^{(0,2)}\rangle - \langle \psi^{(0,1)}|D_0 - E^{(0)}S_0|\psi^{(2,1)}\rangle - E^{(0,1)}\langle \psi^{(0)}|S_2|\psi^{(0,1)}\rangle - E^{(0,2)}\{\langle \psi^{(0)}|S_2|\psi^{(0)}\rangle + \langle \psi^{(0)}|S_0|\psi^{(2,0)}\rangle\} - E^{(2,1)}\langle \psi^{(0)}|S_0|\psi^{(0,1)}\rangle$$
$$= 2\,\mathrm{Re}\langle \psi^{(2,0)}|\Omega - E^{(0,1)}S_0|\psi^{(0,1)}\rangle + \langle \psi^{(0,1)}|D_2 - E^{(0)}S_2 - E^{(2,0)}S_0|\psi^{(0,1)}\rangle - E^{(2,1)}2\,\mathrm{Re}\langle \psi^{(0)}|S_0|\psi^{(0,1)}\rangle - E^{(0,2)}\{2\,\mathrm{Re}\langle \psi^{(0)}|S_0|\psi^{(2,0)}\rangle + \langle \psi^{(0)}|S_2|\psi^{(0)}\rangle\} - E^{(0,1)}2\,\mathrm{Re}\langle \psi^{(0)}|S_2|\psi^{(0,1)}\rangle$$
$$= 2\,\mathrm{Re}\Big\{\langle \varphi^{(2,0)}|\vec{\sigma}\vec{A}|\chi^{(0,1)}\rangle + \langle \chi^{(2,0)}|\vec{\sigma}\vec{A}|\varphi^{(0,1)}\rangle\Big\} - E^{(0,1)}2\,\mathrm{Re}\{\langle \varphi^{(2,0)}|\varphi^{(0,1)}\rangle + \langle \chi^{(0,1)}|\chi^{(0)}\rangle\} + \langle \chi^{(0,1)}|V - E^{(0)}|\chi^{(0,1)}\rangle - E^{(2,0)}\langle \varphi^{(0,1)}|\varphi^{(0,1)}\rangle - E^{(0,2)}\langle \chi^{(0)}|\chi^{(0)}\rangle. \quad (99)$$

The expression in terms of the χ and φ holds for the intermediate normalization.

The only difference in the unitary normalization is that the term containing $E^{(0,2)}$ is absent.

One can further eliminate $\chi^{(0,1)}$ and $\chi^{(2,0)}$ and apply the turnover rule with the necessary precautions; in the intermediate normalization this leads to

$$E^{(2,2)} = \frac{1}{m}\mathrm{Re}\Big\{\langle \varphi^{(2,0)}|A^2|\varphi^{(0)}\rangle + \langle \varphi^{(2,0)}|[(\vec{\sigma}\vec{A}), \big(\vec{\sigma}\vec{p}\big)]_+|\varphi^{(0,1)}\rangle\Big\} + \frac{1}{2m^2}\mathrm{Re}\Big\{\langle \varphi^{(0)}|\vec{\sigma}\vec{p}(V - E^{(0)})\vec{\sigma}\vec{A} + \vec{\sigma}\vec{A}(V - E^{(0)})\vec{\sigma}\vec{p}|\varphi^{(0,1)}\rangle + \frac{1}{4m^2}\Big\{\langle \varphi^{(0)}|\vec{\sigma}\vec{A}(V - E^{(0)})\vec{\sigma}\vec{A}|\varphi^{(0)}\rangle + \langle \varphi^{(0,1)}|\vec{\sigma}\vec{p}(V - E^{(0)})\vec{\sigma}\vec{p}|\varphi^{(0,1)}\rangle\Big\} - 2\,\mathrm{Re}\,E^{(0,1)}\Big\{\langle \varphi^{(2,0)}|\varphi^{(0,1)}\rangle + \frac{1}{4m^2}\langle \varphi^{(0)}|\big(\vec{\sigma}\vec{p}\big)(\vec{\sigma}\vec{A})|\varphi^{(0)}\rangle + \frac{1}{2m}\langle \varphi^{(0)}|T|\varphi^{(0,1)}\rangle\Big\} - E^{(2,0)}\langle \varphi^{(0,1)}|\varphi^{(0,1)}\rangle - E^{(0,2)}\frac{1}{2m}\langle \varphi^{(0)}|T|\varphi^{(0)}\rangle. \quad (100)$$

Further reformulations as for $E^{(2,1)}$ are possible, giving rise to spin-dependent and spin-independent terms.

Again there is no term containing $E^{(0,2)}$ in the unitary normalization.

We are also interested in the leading relativistic correction to a mixed second-order magnetic property. For its evaluation we need, in addition to

(73)–(83), the mixed equation

$$\begin{aligned}
&(D_0 - E^{(0)}S_0)\psi^{(2,1,1)} \\
&\quad + (D_2 - E^{(0)}S_2 - E^{(2)}S_0)\psi^{(0,1,1)} \\
&\quad + (\Omega_1 - E^{(0,1,0)}S_0)\psi^{(2,0,1)} \\
&\quad + (\Omega_2 - E^{(0,0,1)}S_0)\psi^{(2,1,0)} \\
&\quad - E^{(0,1,1)}S_0\psi^{(2,0,0)} \\
&\quad - (E^{(2,1,0)}S_0 + E^{(0,1,0)}S_2)\psi^{(0,0,1)} \\
&\quad - (E^{(2,0,1)}S_0 - E^{(0,0,1)}S_2)\psi^{(0,1,0)} \\
&\quad - (E^{(2,1,1)}S_0 + E^{(0,1,1)}S_2)\psi^{(0)} = 0. \quad (101)
\end{aligned}$$

From this we get

$$\begin{aligned}
E^{(2,1,1)} = &\langle \psi^{(0)}|D_2 - E^{(0)}S_2 - E^{(2)}S_0|\psi^{(0,1,1)}\rangle \\
&+ \langle \psi^{(0)}|\Omega_1 - E^{(0,1,0)}S_0|\psi^{(2,0,1)}\rangle \\
&+ \langle \psi^{(0)}|\Omega_2 - E^{(0,0,1)}S_0|\psi^{(2,1,0)}\rangle \\
&- E^{(2,1,0)}\langle \psi^{(0)}|S_0|\psi^{(0,0,1)}\rangle \\
&- E^{(2,0,1)}\langle \psi^{(0)}|S_0|\psi^{(0,1,0)}\rangle \\
&- E^{(0,1,1)}\{\langle \psi^{(0)}|S_0|\psi^{(2,0,0)}\rangle \\
&+ \langle \psi^{(0)}|S_2|\psi^{(0)}\rangle\} \\
&- E^{(0,0,1)}\langle \psi^{(0)}|S_2|\psi^{(0,1,0)}\rangle \\
&- E^{(0,1,0)}\langle \psi^{(0)}|S_2|\psi^{(0,0,1)}\rangle. \quad (102)
\end{aligned}$$

As in (99) we try to eliminate the doubly perturbed wave functions $\psi^{(0,1,1)}$, $\psi^{(2,1,0)}$, and $\psi^{(2,0,1)}$:

$$\begin{aligned}
E^{(2,1,1)} = &-\langle \psi^{(2,0,0)}|D_0 - E^{(0)}S_0|\psi^{(0,1,1)}\rangle \\
&-\langle \psi^{(0,1,0)}|D_0 - E^{(0)}S_0|\psi^{(2,0,1)}\rangle \\
&-\langle \psi^{(0,0,1)}|D_0 - E^{(0)}S_0|\psi^{(2,1,0)}\rangle \\
&- E^{(0,1,0)}\langle \psi^{(0)}|S_2|\psi^{(0,0,1)}\rangle \\
&- E^{(0,0,1)}\langle \psi^{(0)}|S_2|\psi^{(0,1,0)}\rangle \\
&- E^{(0,1,1)}\{\langle \psi^{(0)}|S_0|\psi^{(2,0,0)}\rangle \\
&+ \langle \psi^{(0)}|S_2|\psi^{(0)}\rangle\} \\
&- E^{(2,1,0)}\langle \psi^{(0)}|S_0|\psi^{(0,0,1)}\rangle \\
&- E^{(2,0,1)}\langle \psi^{(0)}|S_0|\psi^{(0,1,0)}\rangle \\
= &\, 2\,\mathrm{Re}\langle \psi^{(2,0,0)}|\Omega_1 - E^{(0,1,0)}S_0|\psi^{(0,0,1)}\rangle \\
&+ 2\,\mathrm{Re}\langle \psi^{(2,0,0)}|\Omega_2 - E^{(0,0,1)}S_0|\psi^{(0,1,0)}\rangle \\
&+ 2\,\mathrm{Re}\langle \psi^{(0,1,0)}|D_2 - E^{(0)}S_2 \\
&- E^{(2,0,0)}S_0|\psi^{(0,0,1)}\rangle \\
&- E^{(0,0,1)}2\,\mathrm{Re}\langle \psi^{(0,1,0)}|S_2|\psi^{(0)}\rangle \\
&- E^{(0,1,0)}2\,\mathrm{Re}\langle \psi^{(0,0,1)}|S_2|\psi^{(0)}\rangle \\
&- E^{(0,1,1)}\{2\,\mathrm{Re}\langle \psi^{(0)}|S_0|\psi^{(2,0,0)}\rangle \\
&+ \langle \psi^{(0)}|S_2|\psi^{(0)}\rangle\} \\
&- E^{(2,0,1)}2\,\mathrm{Re}\langle \psi^{(0)}|S_0|\psi^{(0,1,0)}\rangle \\
&- E^{(2,1,0)}2\,\mathrm{Re}\,\langle \psi^{(0)}|S_0|\psi^{(0,0,1)}\rangle. \quad (103)
\end{aligned}$$

For practical purposes this expression is not very convenient, because for each nucleus the corresponding perturbative function $\psi^{(0,0,1)}$ needs to be evaluated and the $\psi^{(0,0,1)}$ are singular. It is better to eliminate $\psi^{(0,0,1)}$, $\psi^{(0,1,1)}$, and $\psi^{(2,0,1)}$, but keep $\psi^{(2,1,0)}$.

After some rearrangement, using (74) one gets

$$\begin{aligned}
E^{(2,1,1)} = &\, 2\,\mathrm{Re}\langle \psi^{(2,1,0)}|\Omega_2 - E^{(0,0,1)}S_0|\psi^{(0)}\rangle \\
&+ 2\,\mathrm{Re}\langle \psi^{(2,0,0)}|\Omega_2 - E^{(0,0,1)}S_0|\psi^{(0,1,0)}\rangle \\
&- E^{(0,0,1)}2\,\mathrm{Re}\langle \psi^{(0,1,0)}|S_2|\psi^{(0)}\rangle \\
&- E^{(0,1,1)}\{2\,\mathrm{Re}\langle \psi^{(0)}|S_0|\psi^{(2,0,0)}\rangle \\
&+ \langle \psi^{(0)}|S_2|\psi^{(0)}\rangle\} \\
&- E^{(2,0,1)}2\,\mathrm{Re}\langle \psi^{(0)}|S_0|\psi^{(0,1,0)}\rangle, \quad (104)
\end{aligned}$$

or in terms of the components,

$$\begin{aligned}
E^{(2,1,1)} = &\, 2\,\mathrm{Re}\Big\{\langle \chi^{(2,1,0)}|\vec{\sigma}\vec{A}_2|\varphi^{(0)}\rangle \\
&+ \langle \varphi^{(2,1,0)}|\vec{\sigma}\vec{A}_2|\chi^{(0)}\rangle\Big\} \\
&+ 2\,\mathrm{Re}\Big\{\langle \chi^{(2,0,0)}|\vec{\sigma}\vec{A}_2|\varphi^{(0,1,0)}\rangle \\
&+ \langle \varphi^{(2,0,0)}|\vec{\sigma}\vec{A}_2|\chi^{(0,1,0)}\rangle\Big\} \\
&- E^{(0,0,1)}2\,\mathrm{Re}\,\{\langle \varphi^{(2,0,0)}|\varphi^{(0,1,0)}\rangle \\
&+ \langle \varphi^{(2,1,0)}|\varphi^{(0)}\rangle + \langle \chi^{(0,1,0)}|\chi^{(0)}\rangle\} \\
&- E^{(0,1,1)}\{2\,\mathrm{Re}\langle \varphi^{(0)}|\varphi^{(2,0,0)}\rangle \\
&+ \langle \chi^{(0)}|\chi^{(0)}\rangle\} \\
&- E^{(2,0,1)}2\,\mathrm{Re}\langle \varphi^{(0)}|\varphi^{(0,1,0)}\rangle. \quad (105)
\end{aligned}$$

This still holds in either normalization. In the unitary normalization all terms involving $E^{(0,0,1)}$, $E^{(0,1,1)}$, and $E^{(2,0,1)}$ vanish. In the intermediate normalization for the large component the sum of these terms is

$$\begin{aligned}
&- E^{(0,0,1)}2\,\mathrm{Re}\{\langle \varphi^{(2,0,0)}|\varphi^{(0,1,0)}\rangle + \langle \chi^{(0,1,0)}|\chi^{(0)}\rangle\} \\
&\quad - E^{(0,1,1)}\langle \chi^{(0)}|\chi^{(0)}\rangle. \quad (106)
\end{aligned}$$

Eliminating the χ one finally gets in the intermediate normalization

$$\begin{aligned}E^{(2,1,1)} = {} & \frac{1}{m}\mathrm{Re}\langle \varphi^{(2,1,0)}|[\vec{\sigma}\vec{p}, \vec{\sigma}\vec{A}_2]_+|\varphi^{(0)}\rangle \\ & + \frac{1}{2m^2}\mathrm{Re}\langle \varphi^{(0,1,0)}|\vec{\sigma}\vec{p}(V - E^{(0)})\vec{\sigma}\vec{A}_2 \\ & + \vec{\sigma}\vec{A}_2(V - E^{(0)})\vec{\sigma}\vec{p}|\varphi^{(0)}\rangle \\ & + \frac{1}{2m^2}\mathrm{Re}\langle \varphi^{(0)}|\vec{\sigma}\vec{A}_1(V - E^{(0)})\vec{\sigma}\vec{A}_2|\varphi^{(0)}\rangle \\ & + \frac{1}{m}\mathrm{Re}\langle \varphi^{(2,0,0)}|[\vec{\sigma}\vec{A}_1, \vec{\sigma}\vec{A}_2]_+|\varphi^{(0)}\rangle \\ & + \frac{1}{m}\mathrm{Re}\langle \varphi^{(2,0,0)}|[\vec{\sigma}\vec{p}, \vec{\sigma}\vec{A}_2]_+|\varphi^{(0,1,0)}\rangle \\ & - \frac{1}{2m^2}E^{(0,1,0)}\mathrm{Re}\langle \varphi^{(0)}|\left(\vec{\sigma}\vec{p}\right)\left(\vec{\sigma}\vec{A}_2\right)|\varphi^{(0)}\rangle \\ & - E^{(0,0,1)}2\,\mathrm{Re}\Bigg\{\langle \varphi^{(2,0,0)}|\varphi^{(0,1,0)}\rangle \\ & + \frac{1}{4m^2}\langle \varphi^{(0)}|\left(\vec{\sigma}\vec{A}_1\right)\left(\vec{\sigma}\vec{p}\right)|\varphi^{(0)}\rangle \\ & + \frac{1}{2m}\langle \varphi^{(0,1,0)}|T|\varphi^{(0)}\rangle\Bigg\} \\ & - \frac{1}{2m}E^{(0,1,1)}\langle \varphi^{(0)}|T|\varphi^{(0)}\rangle. \end{aligned} \tag{107}$$

The terms involving $E^{(0,0,1)}$ and $E^{(0,1,1)}$ vanish in the unitary normalization.

SECOND-ORDER [$O(c^4)$] RELATIVISTIC CORRECTIONS

We now need the equations

$$\begin{aligned} & (D_0 - E^{(0)}S_0)\varphi^{(4,0)} \\ & \quad + (D_2 - E^{(0)}S_2 - E^{(2,0)}S_0)\psi^{(2,0)} \\ & \quad - (E^{(2,0)}S_2 + E^{(4,0)}S_0)\psi^{(0)} = 0, \end{aligned} \tag{108}$$

$$\begin{aligned} & (D_0 - E^{(0)}S_0)\psi^{(4,1)} + (D_2 - E^{(0)}S_2 - E^{(2,0)}S_0)\psi^{(2,1)} \\ & \quad - (E^{(2,0)}S_2 + E^{(4,0)}S_0)\psi^{(0,1)} \\ & \quad + (\Omega - E^{(0,1)}S_0)\psi^{(4,0)} \\ & \quad - (E^{(0,1)}S_2 + E^{(2,1)}S_0)\psi^{(2,0)} \\ & \quad - (E^{(2,1)}S_2 + E^{(4,1)}S_0)\psi^{(0)} = 0, \end{aligned} \tag{109}$$

$$\begin{aligned} & (D_0 - E^{(0)}S_0)\psi^{(4,2)} + (D_2 - E^{(0)}S_2 - E^{(2,0)}S_0)\psi^{(2,2)} \\ & \quad - (E^{(2,0)}S_2 + E^{(4,0)}S_0)\psi^{(0,2)} \\ & \quad + (\Omega - E^{(0,1)}S_0)\psi^{(4,1)} \\ & \quad - (E^{(0,1)}S_2 + E^{(2,1)}S_0)\psi^{(2,1)} \\ & \quad - (E^{(2,1)}S_2 + E^{(4,1)}S_0)\psi^{(0,1)} \\ & \quad - E^{(0,2)}S_0\psi^{(4,0)} - (E^{(0,2)}S_2 + E^{(2,2)}S_0)\psi^{(2,0)} \\ & \quad - (E^{(2,2)}S_2 + E^{(4,2)}S_0)\psi^{(0)} = 0, \end{aligned} \tag{110}$$

from which we get

$$\begin{aligned} E^{(4,0)} = {} & \langle \psi^{(0)}|D_2 - E^{(0)}S_2 - E^{(2,0)}S_0|\psi^{(2,0)}\rangle \\ & - E^{(2,0)}\langle \psi^{(0)}|S_2|\psi^{(0)}\rangle \\ = {} & \langle \chi^{(0)}|V - E^{(0)}|\chi^{(2,0)}\rangle - E^{(2,0)}\langle \chi^{(0)}|\chi^{(0)}\rangle. \end{aligned} \tag{111}$$

The last line is correct in the intermediate normalization. In the unitary normalization it must be replaced by

$$\begin{aligned} E^{(4,0)} = {} & \langle \chi^{(0)}|V - E^{(0)}|\chi^{(2,0)}\rangle \\ & - \frac{1}{2}E^{(2,0)}\langle \chi^{(0)}|\chi^{(0)}\rangle; \end{aligned} \tag{112}$$

$$\begin{aligned} E^{(4,1)} = {} & \langle \psi^{(0)}|D_2 - E^{(0)}S_2 - E^{(2,0)}S_0|\psi^{(2,1)}\rangle \\ & + \langle \psi^{(0)}|\Omega - E^{(0,1)}S_0|\psi^{(4,0)}\rangle \\ & - E^{(4,0)}\langle \psi^{(0)}|S_0|\psi^{(0,1)}\rangle \\ & - E^{(2,1)}\{\langle \psi^{(0)}|S_0|\psi^{(2,0)}\rangle + \langle \psi^{(0)}|S_2|\psi^{(0)}\rangle\} \\ & - E^{(2,0)}\langle \psi^{(0)}|S_2|\psi^{(0,1)}\rangle \\ & - E^{(0,1)}\langle \psi^{(0)}|S_2|\psi^{(2,0)}\rangle \\ = {} & -\langle \psi^{(2,0)}|D_0 - E^{(0)}S_0|\psi^{(2,1)}\rangle \\ & - E^{(4,0)}\langle \psi^{(0)}|S_0|\psi^{(0,1)}\rangle \\ & - E^{(2,0)}\langle \psi^{(0)}|S_2|\psi^{(0,1)}\rangle \\ & - \langle \psi^{(0,1)}|D_0 - E^{(0)}S_0|\psi^{(4,0)}\rangle \\ & - E^{(0,1)}\langle \psi^{(0)}|S_2|\psi^{(2,0)}\rangle \\ & - E^{(2,1)}\{\langle \psi^{(0)}|S_2|\psi^{(0)}\rangle \\ & + \langle \psi^{(0)}|S_0|\psi^{(2,0)}\rangle\} \\ = {} & 2\,\mathrm{Re}\langle \psi^{(2,0)}|D_2 - E^{(0)}S_2|\psi^{(0,1)}\rangle \\ & + \langle \psi^{(2,0)}|\Omega|\psi^{(2,0)}\rangle \\ & - E^{(4,0)}2\,\mathrm{Re}\langle \psi^{(0,1)}|S_0|\psi^{(0)}\rangle \\ & - E^{(2,1)}\{2\,\mathrm{Re}\langle \psi^{(0)}|S_0|\psi^{(2,0)}\rangle \\ & + \langle \psi^{(0)}|S_2|\psi^{(0)}\rangle\} \\ & - E^{(2,0)}2\,\mathrm{Re}\{\langle \psi^{(0)}|S_2|\psi^{(0,1)}\rangle \\ & + \langle \psi^{(0,1)}|S_0|\psi^{(2,0)}\rangle\} \\ & - E^{(0,1)}\{2\,\mathrm{Re}\langle \psi^{(2,0)}|S_2|\psi^{(0)}\rangle \\ & + \langle \psi^{(2,0)}|S_0|\psi^{(2,0)}\rangle\}. \end{aligned} \tag{113}$$

The normalization is not specified. We renounce on giving the expression in terms of upper and lower components and *a fortiori* on the elimination of the lower components. This last step is elementary but tedious and leads to rather lengthy expressions. For $E^{(4,2)}$ we get from (110)

$$\begin{aligned}E^{(4,2)} = &\langle\psi^{(0)}|D_2 - E^{(0)}S_2 - E^{(2,0)}S_0|\psi^{(2,2)}\rangle\\ &+\langle\psi^{(0)}|\Omega - E^{(0,1)}S_0|\psi^{(4,1)}\rangle\\ &-\langle\psi^{(0)}|E^{(2,0)}S_2 + E^{(4,0)}S_0|\psi^{(0,2)}\rangle\\ &-\langle\psi^{(0)}|E^{(0,1)}S_2 + E^{(2,1)}S_0|\psi^{(2,1)}\rangle\\ &-\langle\psi^{(0)}|E^{(2,1)}S_2 + E^{(4,1)}S_0|\psi^{(0,1)}\rangle\\ &-E^{(0,2)}\langle\psi^{(0)}|S_0|\psi^{(4,0)}\rangle\\ &-\langle\psi^{(0)}|E^{(0,2)}S_2 + E^{(2,2)}S_0|\psi^{(2,0)}\rangle\\ &-\langle\psi^{(0)}|E^{(2,2)}S_2|\psi^{(0)}\rangle. \qquad (114)\end{aligned}$$

It is relatively easy to eliminate $\psi^{(2,2)}$ and $\psi^{(4,1)}$ with the result

$$\begin{aligned}E^{(4,2)} = &\langle\psi^{(2,0)}|D_2 - E^{(0)}S_2 - E^{(2,0)}S_0|\psi^{(0,2)}\rangle\\ &+\langle\psi^{(0,1)}|D_2 - E^{(0)}S_2 - E^{(2,0)}S_0|\psi^{(2,1)}\rangle\\ &+\langle\psi^{(2,0)}|\Omega - E^{(0,1)}S_0|\psi^{(2,1)}\rangle\\ &+\langle\psi^{(0,1)}|\Omega - E^{(0,1)}S_0|\psi^{(4,0)}\rangle\\ &-E^{(4,1)}2\,\mathrm{Re}\langle\psi^{(0,1)}|S_0|\psi^{(0)}\rangle\\ &-E^{(4,0)}\{\langle\psi^{(0,1)}|S_0|\psi^{(0,1)}\rangle\\ &+\langle\psi^{(0)}|S_0|\psi^{(0,2)}\rangle\}\\ &-E^{(2,1)}\{2\,\mathrm{Re}\langle\psi^{(0,1)}|S_0|\psi^{(2,0)}\rangle\\ &+2\,\mathrm{Re}\langle\psi^{(0,1)}|S_2|\psi^{(0)}\rangle\\ &+\langle\psi^{(0)}|S_0|\psi^{(2,1)}\rangle\}\\ &-E^{(2,2)}\{2\,\mathrm{Re}\langle\psi^{(2,0)}|S_0|\psi^{(0)}\rangle\\ &+\langle\psi^{(0)}|S_2|\psi^{(0)}\rangle\}\\ &-E^{(0,2)}\{2\,\mathrm{Re}\langle\psi^{(2,0)}|S_2|\psi^{(0)}\rangle\\ &+\langle\psi^{(2,0)}|S_0|\psi^{(2,0)}\rangle\\ &+\langle\psi^{(0)}|S_0|\psi^{(4,0)}\rangle\}\\ &-E^{(0,1)}\{2\,\mathrm{Re}\langle\psi^{(2,0)}|S_2|\psi^{(0,1)}\rangle\\ &+\langle\psi^{(0)}|S_2|\psi^{(2,1)}\rangle\}\\ &-E^{(2,0)}\{\langle\psi^{(0)}|S_2|\psi^{(0,2)}\rangle\\ &+\langle\psi^{(0,1)}|S_2|\psi^{(0,1)}\rangle\}. \qquad (115)\end{aligned}$$

One can further eliminate either $\psi^{(0,2)}$ or $\psi^{(4,0)}$. Anyway, the final expressions become very lengthy, which is generally hard to avoid in multiple perturbation theory to higher order.

STATIONARY MULTIPLE PERTURBATION THEORY: REGULARIZATION OF TRIAL FUNCTIONS

So far we have assumed that the unperturbed Schrödinger equation and the inhomogeneous differential equations of perturbation theory are both solved exactly. However, this is usually not possible. In fact, one finds approximate solutions by making certain functionals stationary.

The stationary formulation of DPT in the absence of a magnetic field has been described elsewhere in detail.[15] One starts from the energy expectation value and expands this, as well as its stationary condition, in powers of c^{-1}. To zeroth order in c^{-1} one gets the stationarity condition corresponding to the Lévy–Leblond equation and to $O(c^{-2})$ the Hylleraas–Rutkowski functional that is to be made stationary with respect to the variation of $\varphi^{(2,0)}$ and $\chi^{(2,0)}$. Of course, the Dirac equation is not bounded from below and there is no automatic guarantee that minimization of the respective functionals will approach the exact expression from below. This can be guaranteed, however, if one chooses[7,8,26]

$$\chi = X\varphi \qquad (116)$$

with X satisfying the implicit equation.

$$X = \frac{1}{2mc^2}\left\{c\vec{\sigma}\vec{p} + [V, X] - cX\vec{\sigma}\vec{p}X\right\}. \qquad (117)$$

However, this condition for electronic (rather than positronic) states can be applied safely only if the trial functions $\tilde{\varphi}$ and $\tilde{\chi}$ have the correct behavior at the position of a nucleus, where the exact φ and χ have weak singularities of the type

$$\tilde{\varphi} \sim r^{\nu}; \quad \tilde{\chi} \sim r^{\nu}; \quad \nu = \sqrt{1 - Z^2/c^2} - 1. \qquad (118)$$

If one chooses $\tilde{\varphi}$ regular at $r = 0$ and applies (116) naively, one introduces spurious strong singularities into $\tilde{\chi}$, which make the stationary approach divergent. The solution to this problem is to choose $\tilde{\chi}$ regular at $r = 0$, if one chooses $\tilde{\varphi}$ so. Then, however, one can no longer satisfy (116) exactly but only in the mean in a Hilbert space sense. As a consequence, one loses the property that one is slightly above the exact electronic ground state. But this is a minor defect with which one can easily live. If one has selected a regular basis $\{\varphi_k\}$

for the expansion of $\tilde{\varphi}$, then one must use the basis $\{\chi_k\} = \{\frac{1}{2m}\vec{\sigma}\vec{p}\varphi_k\}$ for the expansion of $\tilde{\chi}$ in the sense of the generalized kinetic balance condition.

A modification is necessary in the presence of a magnetic field. Then the basis for the expansion of $\tilde{\chi}$ must not only contain $\{\frac{1}{2m}\vec{\sigma}\vec{p}\varphi_k\}$, but also $\{\frac{1}{2m}\vec{\sigma}\vec{A}\varphi_k\}$. A $\vec{\sigma}\vec{p}$ basis and a $\vec{\sigma}\vec{A}$ basis are both needed. These partial basis sets have different transformation properties and one cannot take the role of the other.

The weak singularities of the eigenfunctions of the Dirac operator in the presence of the Coulomb potential of a point charge are well understood and can be controlled in a straightforward way.[15]

More serious are the consequences of the singularity of the magnetic field of a point nucleus. This singularity already caused difficulties in the nonrelativistic theory, and it is unlikely that the Schrödinger equation in the presence of the magnetic field of a point magnetic moment has a solution. First-order perturbation theory can nevertheless be justified, even if all higher orders diverge. The situation is probably not simpler in the relativistic context. As already mentioned, one has to abandon the approximation of a magnetic point dipole if one wants to go to higher orders.[12]

Effective Hamiltonian Formulation

GENERAL CONSIDERATIONS

Earlier we essentially considered a single nondegenerate one-electron state. The formalism can be applied to degenerate states as well, provided that one starts with perturbation adapted states, which diagonalize the first-order perturbations. This means we have to first construct states that are adapted to the relativistic perturbation (i.e., are irreducible representations of the double groups) and the magnetic field (eigenfunctions of S_z), which is rather inconvenient. In the more general degenerate or even quasidegenerate situation it is better to shift from a single state to a manifold of states characterized by a *model space* $\{\varphi_k^{(0)}\}$ of unperturbed states and an effective Hamiltonian L that is constructed from the Dirac operator (in the magnetic field) by means of a unitary transformation U,

$$L = U^{\dagger}DU, \tag{119}$$

such that the eigenvalues of L in a matrix representation in the model space yield the exact eigenvalues corresponding to the model space. Such a transformation was recently presented for the Dirac equation without a magnetic field,[6] and we give now the generalization to the case with a magnetic field. For an alternative quasidegenerate formulation see refs. 27 and 28.

Because L should act on two-component spinors but D on four-component spinors, the transformation U must be of the form

$$U = \begin{pmatrix} U^g \\ U^f \end{pmatrix}, \tag{120}$$

where U^g and U^f are both operators that act on two-component spinors. To treat electronic states (rather than positronic ones or a mixture) a relation between U^g and U^f must hold in the absence of a magnetic field,

$$U^f = XU^g, \tag{121}$$

with X satisfying (117).[7,26] In the presence of a magnetic field this must be changed to

$$U^f = YU^g, \tag{122}$$

$$2mc^2Y = c\vec{\sigma}\cdot\left(\vec{p} + \lambda\vec{A}\right) - [Y, V] - cY\vec{\sigma}\cdot\left(\vec{p} + \lambda\vec{A}\right)Y. \tag{123}$$

It is convenient to make the same change of the metric as in DPT and to define

$$\tilde{Y} = cY; \quad \tilde{U} = \begin{pmatrix} U^g \\ \tilde{U}^f \end{pmatrix}; \quad \tilde{U}^f = \tilde{Y}U^g; \tag{124}$$

$$\tilde{D} = \begin{pmatrix} 1 & \\ & c^{-1} \end{pmatrix}\begin{pmatrix} V & c\vec{\sigma}\vec{p} \\ c\vec{\sigma}\vec{p} & V - 2mc^2 \end{pmatrix}\begin{pmatrix} 1 & \\ & c^{-1} \end{pmatrix} = D_0 + c^{-2}D_2. \tag{125}$$

The transformed Hamiltonian is then

$$L = (U^{g\dagger}, U^{g\dagger}\tilde{Y}^{\dagger})(D_0 + c^{-2}D_2 + \lambda\Omega)\begin{pmatrix} U^g \\ \tilde{Y}U^g \end{pmatrix}. \tag{126}$$

We require that L is ''diagonal'':

$$L = L_D = \varrho L\varrho + (1 - \varrho)L(1 - \varrho), \tag{127}$$

$$L_N = \varrho L(1 - \varrho) + (1 - \varrho)L\varrho = 0, \tag{128}$$

where ϱ is the projector to the model space.

The diagonality condition (128) can also be written as

$$\langle\varphi_i^{(0)}|L|\varphi_a^{(0)}\rangle = \langle\varphi_a^{(0)}|L|\varphi_i^{(0)}\rangle = 0 \tag{129}$$

for $\varphi_i^{(0)}$ in the model space and $\varphi_a^{(0)}$ outside the model space, the $\varphi_i^{(0)}$ and $\varphi_a^{(0)}$ forming an orthonormalset. We henceforth use $\varphi_i^{(0)}$ and $\varphi_a^{(0)}$ with this meaning.

For products of operators the even-odd rule holds[29,30]:

$$D \times D = N \times N = D, \tag{130}$$

$$D \times N = N \times D = N; \tag{131}$$

i.e., the prouct of a diagonal and a nondiagonal operator is nondiagonal, while the product of two operators of the same type is diagonal.

DOUBLE PERTURBATION EXPANSION

The effective Hamiltonian is then the projection of L onto the model space:

$$L_C = \varrho L \varrho, \tag{132}$$

where the subscript C stands for closed. We expand (126) in powers of c^{-1} and λ:

$$L = \sum_{\mu,\nu} c^{-2\mu} \lambda^{\nu} L_{2\mu,\nu}. \tag{133}$$

The expansion of $\tilde{Y}$ in powers of c^{-1} and λ leads to

$$\tilde{Y} = cY = Y_0 + \lambda Y_{01} + \lambda^2 Y_{02} + c^{-2} Y_{20} + c^{-2}\lambda Y_{21} + \cdots, \tag{134}$$

$$Y_0 = \frac{1}{2m} \vec{\sigma}\vec{p}, \tag{135}$$

$$Y_{01} = \frac{1}{2m} \vec{\sigma}\vec{A}, \tag{136}$$

$$Y_{02} = 0, \tag{137}$$

$$Y_{20} = \frac{1}{2m}[V, Y_0] - (Y_0)^3 = \frac{1}{2m}\{VY_0 - Y_0 H_0\}, \tag{138}$$

$$Y_{21} = \frac{1}{2m}[V, Y_{01}] - Y_{01}(Y_0)^2 - Y_0 Y_{01} Y_0 - (Y_0)^2 Y_{01} = \frac{1}{2m}\{VY_{01} - Y_{01}H_0\} - Y_0 Y_{01} Y_0 - (Y_0)^2 Y_{01}, \tag{139}$$

$$Y_{22} = -(Y_{01})^2 Y_0 - Y_{01} Y_0 Y_{01} - Y_0 (Y_{01})^2, \tag{140}$$

$$Y_{40} = \frac{1}{2m}[V, Y_{20}] - (Y_0)^2 Y_{20} - Y_{20}(Y_0)^2. \tag{141}$$

For U there is the (unitary) normalization condition

$$U^\dagger U = U^{g\dagger}(1 + Y^\dagger Y) U^g = U^{g\dagger}(1 + c^{-2}\tilde{Y}^\dagger \tilde{Y}) U^g = 1 \tag{142}$$

with the expansion

$$U_0^{g\dagger} U_0^g = 1, \tag{143}$$

$$U_0^{g\dagger} U_{01}^g + U_{01}^{g\dagger} U_0^g = 0, \tag{144}$$

$$U_{20}^{g\dagger} U_0^g + U_0^{g\dagger} U_{20}^g + U_0^{g\dagger} Y_0^\dagger Y_0 U_0^g = 0 \ldots. \tag{145}$$

It is no loss of generality to choose

$$U_0^g = 1. \tag{146}$$

Hence,

$$U_{01}^{g\dagger} + U_{01}^g = 0, \tag{147}$$

$$U_{20}^{g\dagger} + U_{20}^g + (Y_0)^2 = 0, \tag{148}$$

$$U_{02}^g + U_{02}^{g\dagger} + U_{01}^{g\dagger} U_{01}^g = 0, \tag{149}$$

$$U_{21}^{g^\dagger} + U_{21}^g + U_{20}^{g\dagger} U_{01}^g + U_{01}^{g\dagger} U_{20}^g + U_0^{f\dagger} U_{01}^f + U_{01}^{f\dagger} U_0^f = U_{21}^{g\dagger} + U_{21}^g + U_{20}^{g\dagger} U_{01}^g + U_{01}^{g\dagger} U_{20}^g + Y_0^2 U_{01}^g + Y_0 Y_{01} + Y_{01} Y_0 + U_{01}^{g\dagger} Y_0^2 = 0 \ldots. \tag{150}$$

For $\tilde{U}^\dagger \tilde{D} \tilde{U}$ we get

$$\begin{aligned}
\tilde{U}^\dagger \tilde{D}\, \tilde{U} &= U^{g\dagger}\Big\{V + \tilde{Y}^\dagger\big(\vec{\sigma}\vec{p} + \lambda\vec{\sigma}\vec{A}\big) \\
&\quad + \big(\vec{\sigma}\vec{p} + \lambda\vec{\sigma}\vec{A}\big)\tilde{Y} \\
&\quad - 2m\tilde{Y}^\dagger \tilde{Y} + c^{-2}\tilde{Y}^\dagger V \tilde{Y}\Big\} U^g \\
&= U^{g\dagger}\Big\{V + 2m\tilde{Y}^\dagger(Y_0 + \lambda Y_{01}) \\
&\quad + 2m(Y_0 + \lambda Y_{01})\tilde{Y} \\
&\quad - 2m\tilde{Y}^\dagger \tilde{Y} + c^{-2}\tilde{Y}^\dagger V \tilde{Y}\Big\} U^g \\
&= U^{g\dagger}\Big\{H - 2m\big(\tilde{Y} - Y_0 - \lambda Y_{01}\big)^\dagger \\
&\quad \times \big(\tilde{Y} - Y_0 - \lambda Y_{01}\big) + c^{-2}\tilde{Y}^\dagger V \tilde{Y}\Big\} U^g \\
&= H + \frac{1}{2}\{U^{g\dagger}[H, U^g] + [U^{g\dagger}, H] U^g\} \\
&\quad - \frac{1}{2} c^{-2} [U^{g\dagger}\tilde{Y}^\dagger \tilde{Y}\, U^g, H]_+ \\
&\quad + U^{g\dagger}\Big\{c^{-2}\tilde{Y}^\dagger V \tilde{Y} - 2m\big(\tilde{Y} - Y_0 - \lambda Y_{01}\big)^\dagger \\
&\quad \times \big(\tilde{Y} - Y_0 - \lambda Y_{01}\big)\Big\} U^g
\end{aligned} \tag{151}$$

with

$$H = V + \frac{1}{2m}\left(\vec{\sigma}\vec{p} + \lambda\vec{\sigma}\vec{A}\right)^2 = H_0 + \lambda H_1 + \lambda^2 H_2; \quad (152)$$

$$H_0 = V + \frac{1}{2m}p^2,$$

$$H_1 = \frac{1}{2m}[\vec{\sigma}\vec{A}, \vec{\sigma}\vec{p}]_+, \quad H_2 = \frac{1}{2m}\vec{A}^2. \quad (153)$$

NONRELATIVISTIC LIMIT

We expand (151) in powers of c^{-1} and λ and get for the lower order terms

$$(\tilde{U}^\dagger\tilde{D}\tilde{U})_0 = H_0, \quad (154)$$

$$(\tilde{U}\tilde{D}\tilde{U})_{01} = H_1 + \frac{1}{2}\left[H_0, U_{01}^g - U_{01}^{g\dagger}\right], \quad (155)$$

$$(\tilde{U}\tilde{D}\tilde{U})_{02} = H_2 + \frac{1}{2}\left\{U_{01}^{g\dagger}[H_0, U_{01}^g] + \left[U_{01}^{g\dagger}, H_0\right]U_{01}^g + \left[H_0, U_{02}^g - U_{02}^{g\dagger}\right] + \left[H_1, U_{01}^g - U_{01}^{g\dagger}\right]\right\}, \quad (156)$$

$$(\tilde{U}\tilde{D}\tilde{U})_{20} = \frac{1}{2}\left\{\left[H_0, U_{20}^g - U_{20}^{g\dagger}\right] - \left[Y_0^2, H_0\right]_+ + 2Y_0 V Y_0\right\}. \quad (157)$$

We used $U_0^g = 1$ and $Y_0^\dagger = Y_0$.

We must determine the U_{pq}^g such that expressions (154)–(157) become diagonal in the sense of (127)–(129). Obviously (154) is already diagonal; hence,

$$(L_C)_0 = \varrho H_0 \varrho. \quad (158)$$

In view of (158) it is convenient to choose the model space functions $\varphi_j^{(0)}$ and the complementary functions $\varphi_a^{(0)}$ as eigenfunctions of H_0 such that H_0 is strictly diagonal and not only block diagonal [i.e., diagonal in the sense that $H_0 = (H_0)_D$].

$$H_0\varphi_p^{(0)} = \varepsilon_p^{(0)}\varphi_p^{(0)}, \quad (159)$$

where $p = i$ or a.

Using the normalization condition (147) we can rewrite (155) as

$$(\tilde{U}\tilde{D}\tilde{U})_{01} = H_1 + [H_0, U_{01}^g]; \quad U_{01}^{g\dagger} = -U_{01}^g. \quad (160)$$

The diagonality condition is then

$$\langle\varphi_i^{(0)}|H_1|\varphi_a^{(0)}\rangle = -(\varepsilon_i^{(0)} - \varepsilon_a^{(0)}) < \varphi_i^{(0)}|U_{01}^g|\varphi_a^{(0)}\rangle, \quad (161)$$

which allows us to construct the nondiagonal elements of U_{01}^g.

For the diagonal part of U_{01}^g we note that the normalization condition requires this to be anti-Hermitian but that an anti-Hermitian diagonal part of U_{01}^g is physically irrelevant (it just implies a phase transformation within the model space[29]) such that it is no loss of generality to choose

$$\langle\varphi_i^{(0)}|U_{01}^g|\varphi_j^{(0)}\rangle = 0. \quad (162)$$

We get L_{01} as the projection of (160) to the model space

$$(L_C)_{01} = \varrho H_1 \varrho. \quad (163)$$

The commutator $[H_0, U_{01}^g]$ does not contribute because the nondiagonal part of U_{01}^g gives rise to a nondiagonal term in view of the even-odd rule, and the diagonal part of U_{01}^g vanishes by virtue of (162). The matrix elements of L_{01} are hence

$$\langle\varphi_i^{(0)}|L_{01}|\varphi_j^{(0)}\rangle = \langle\varphi_i^{(0)}|H_1|\varphi_j^{(0)}\rangle. \quad (164)$$

Diagonality of (156) leads to a condition for the nondiagonal part of $U_{02}^g - U_{02}^{g\dagger}$. If we choose the diagonal part of U_{02}^g as Hermitian, which is again no loss of generality, the commutator $[H_0, U_{02}^g - U_{02}^{g\dagger}]$ does not contribute to L_{02}. We further use

$$[H_0, U_{01}^g] = \left[U_{01}^{g\dagger}, H_0\right] = L_{01} - H_1, \quad (165)$$

which is just the diagonality condition for H_{01}, and insert this into (156). So we get

$$(L_C)_{02} = \varrho H_2 \varrho + \frac{1}{2}\varrho\{U_{01}^{g\dagger}L_{01} + L_{01}U_{01}^g - U_{01}^{g\dagger}H_1 - H_1U_{01}^g + H_1U_{01}^g - U_{01}^gH_1 - H_1U_{01}^{g\dagger} + U_{01}^{g\dagger}H_1\}\varrho = \varrho\left\{H_2 + \frac{1}{2}[H_1, U_{01}^g]\right\}\varrho. \quad (166)$$

By virtue of the even-odd rule the terms involving L_{01} do not contribute. For the matrix elements of

L_{02} in the model space we get

$$\begin{aligned}
&\langle \varphi_i^{(0)}|L_{02}|\varphi_j^{(0)}\rangle \\
&\quad = \langle \varphi_i^{(0)}|H_2|\varphi_j^{(0)}\rangle \\
&\qquad + \frac{1}{2}\langle \varphi_i^{(0)}|H_1 U_{01}^g|\varphi_j^{(0)}\rangle + \frac{1}{2}\langle \varphi_i^{(0)}|U_{01}^{g\dagger} H_1|\varphi_j^{(0)}\rangle \\
&\quad = \langle \varphi_i^{(0)}|H_2|\varphi_j^{(0)}\rangle + \frac{1}{2}\langle \varphi_i^{(0)}|H_1|\varphi_j^{(0,1)}\rangle \\
&\qquad + \frac{1}{2}\langle \varphi_i^{(0,1)}|H_1|\varphi_j^{(0)}\rangle, \qquad (167)
\end{aligned}$$

where we used

$$\varphi_j^{(0,1)} = U_{01}^g \varphi_j^{(0)}. \qquad (168)$$

We use the same notation for the expansion of the relativistic wave functions generated from the model space as we used previously for the expansion of relativistic eigenfunctions. The latter correspond to a special choice of the model space: where the model functions are perturbation adapted.

In the case of two magnetic perturbation we are interested in L_{011}. In an obvious notation we have

$$\begin{aligned}
&(\tilde{U}\tilde{D}\tilde{U})_{011} \\
&\quad = H_{011} + \frac{1}{2}\Big\{U_{010}^{g\dagger}[H_0, U_{001}] + U_{001}^{g\dagger}[H_0, U_{010}] \\
&\qquad + \big[U_{010}^{g\dagger}, H_0\big]U_{001} + \big[U_{001}^{g\dagger}, H_0\big]U_{010} \\
&\qquad + \big[H_0, U_{011}^g - U_{011}^{g\dagger}\big] \\
&\qquad + \big[H_{010}, U_{001}^g - U_{001}^{g\dagger}\big] \\
&\qquad + \big[H_{001}, U_{010}^g - U_{010}^{g\dagger}\big]\Big\}. \qquad (169)
\end{aligned}$$

Transforming this in the same way as (166) we get

$$\begin{aligned}
(L_C)_{011} &= \varrho H_{011}\varrho + \frac{1}{2}\varrho\{[H_{010}, U_{001}^g] \\
&\qquad + [H_{001}, U_{010}^g]\}\varrho. \qquad (170)
\end{aligned}$$

Using further that

$$H_{010} = L_{010} - [H_0, U_{010}^g], \qquad (171)$$

$$H_{001} = L_{001} - [H_0, U_{001}^g], \qquad (172)$$

and that consequently

$$\begin{aligned}
\varrho[H_{010}, U_{010}^g]\varrho &= -\varrho[[H_0, U_{010}^g], U_{001}^g]\varrho \\
&= -\varrho[[H_0, U_{001}^g], U_{010}^g]\varrho \\
&= \varrho[H_{001}, U_{010}^g]\varrho, \qquad (173)
\end{aligned}$$

we get

$$\begin{aligned}
(L_C)_{011} &= \varrho\{H_{011} + [H_{010}, U_{001}^g]\}\varrho \\
&= \varrho\{H_{011} + [H_{001}, U_{010}^g]\}\varrho. \qquad (174)
\end{aligned}$$

LEADING RELATIVISTIC CORRECTIONS

The condition for vanishing of the nondiagonal part of (157) is

$$\begin{aligned}
&\langle \varphi_i^{(0)}|Y_0\left[V - \frac{1}{2}(\varepsilon_i^{(0)} + \varepsilon_a^{(0)})\right]Y_0|\varphi_a^{(0)}\rangle \\
&\quad + \frac{1}{2}(\varepsilon_i^{(0)} - \varepsilon_a^{(0)})\langle \varphi_i^{(0)}|U_{20}^{g\dagger} - U_{20}^g|\varphi_a^{(0)}\rangle = 0, \qquad (175)
\end{aligned}$$

which allows us to construct the nondiagonal elements of $U_{20}^{g\dagger} - U_{20}^g$. For the diagonal elements we use the normalization condition and impose that $(U_{20}^g)_D$ is hermitian.

$$(U_{20}^g)_D = (U_{20}^{g\dagger})_D = -\frac{1}{2}(Y_0^2)_D. \qquad (176)$$

The matrix elements of L_{20} in the model space are

$$\begin{aligned}
&\langle \varphi_i^{(0)}|L_{20}|\varphi_j^{(0)}\rangle \\
&\quad = \langle \varphi_i^{(0)}|Y_0\left[V - \frac{1}{2}\left(\varepsilon_i^{(0)} + \varepsilon_j^{(0)}\right)\right]Y_0|\varphi_j^{(0)}\rangle \\
&\quad = \langle \chi_i^{(0)}|V - \frac{1}{2}\left(\varepsilon_i^{(0)} + \varepsilon_j^{(0)}\right)|\chi_j^{(0)}\rangle. \qquad (177)
\end{aligned}$$

We later use the diagonality condition in the following form:

$$\frac{1}{2}\big[H_0, U_{20}^g - U_{20}^{g\dagger}\big] = L_{20} - Y_0 V Y_0 + \frac{1}{2}\big[Y_0^2, H_0\big]_+, \qquad (178)$$

$$\frac{1}{2}\big[H_0, U_{20}^g + U_{20}^{g\dagger}\big] = -\frac{1}{2}\big[H_0, Y_0^2\big], \qquad (179)$$

$$[H_0, U_{20}^g] = L_{20} - Y_0 V Y_0 + Y_0^2 H_0, \qquad (180)$$

$$-\big[H_0, U_{20}^{g\dagger}\big] = L_{20} - Y_0 V Y_0 + H_0 Y_0^2. \qquad (181)$$

Let us now compare the L_{pq} with the $E^{(p,q)}$ obtained previously. For the case that the model space consists of a single nondegenerate unperturbed function $\varphi_k^{(0)}$, the L matrices reduce to a single term and agree with the corresponding E in unitary normalization.

Otherwise, the L matrices are no longer diagonal, meaning that there are off-diagonal elements $\langle \varphi_i^{(0)}|L|\varphi_k^{(0)}\rangle$ within the model space. On the other

hand, in the perturbed functions like $\varphi^{(0,1)}$ or $\varphi^{(2,0)}$, the sum over virtual functions goes only over those outside the model space. Energy denominators within the model space do not appear.

Let us now come to the relativistic corrections to properties, first to the leading correction to a first-order property.

$$\begin{aligned}(\tilde{U}^\dagger \tilde{D} \tilde{U})_{21} &= \frac{1}{2}\{[H_0, U_{21}^g - U_{21}^{g\dagger}] + U_{20}^{g\dagger}[H_0, U_{01}^g] \\ &+ [U_{20}^{g\dagger}, H_0]U_{01}^g + U_{01}^{g\dagger}[H_0, U_{20}^g] \\ &+ [U_{01}^{g\dagger}, H_0]U_{20}^g + [H_1, U_{20}^g - U_{20}^{g\dagger}]\} \\ &- \frac{1}{2}[U_{01}^{g\dagger} Y_0^2 + Y_0^2 U_{01}^g + Y_{01}Y_0 \\ &+ Y_0 Y_{01}, H_0]_+ - \frac{1}{2}[Y_0^2, H_1]_+ \\ &+ U_{01}^{g\dagger} Y_0 V Y_0 + Y_0 V Y_0 U_{01}^g \\ &+ Y_{01} V Y_0 + Y_0 V Y_{01}. \end{aligned} \tag{182}$$

We first note that $[H_0, U_{21}^g - U_{21}^{g\dagger}]$ does not contribute to L_{21}.

For a further manipulation of this expression we note that U_{01}^g is anti-Hermitian, and we decompose U_{02}^g and $U_{02}^{g\dagger}$ into their Hermitian and non-Hermitian parts:

$$U_{20}^g = U_{20}^h + U_{20}^a, \tag{183}$$

$$U_{20}^{g\dagger} = U_{20}^h - U_{20}^a, \tag{184}$$

$$U_{20}^h = \frac{1}{2}(U_{20}^g + U_{20}^{g\dagger}) = -\frac{1}{2}Y_0^2, \tag{185}$$

$$U_{20}^a = \frac{1}{2}(U_{20}^g - U_{20}^{g\dagger}). \tag{186}$$

This allows a reformulation of (182) to

$$\begin{aligned}(L_C)_{21} = \frac{1}{2}\varrho\Big\{&[[H_0, U_{01}^g], U_{20}^a] + [[H_0, U_{20}^a], U_{01}^g] \\ &- \frac{1}{2}[[H_0, U_{01}^g], Y_0^2]_+ \\ &+ \frac{1}{2}[[H_0, Y_0^2], U_{01}^g]_+ \\ &+ 2[H_1, U_{20}^a] - [[Y_0^2, U_{01}^g], H_0]_+ \\ &- [Y_{01}Y_0 + Y_0 Y_{01}, H_0]_+ - [Y_0^2, H_1]_+ \\ &+ 2[Y_0 V Y_0, U_{01}^g] + 2Y_{01} V Y_0 + 2Y_0 V Y_{01}\Big\}\varrho. \end{aligned} \tag{187}$$

We further see that in view of the Jacobi identity and the stationarity condition for H_0, the first two double commutators are equal. We now consider two reformulations. In the first of these we take twice the second double commutator and use that as a consequence of the diagonality of L_{20}, given by (157):

$$\begin{aligned}\varrho\Big\{&[H_0, U_{20}^g - U_{20}^{g\dagger}], X_N] - [[Y_0^2, H_0]_+, X_N] \\ &+ 2[Y_0 V Y_0, X_N]\Big\}\varrho = 0 \end{aligned} \tag{188}$$

for any nondiagonal X_N, in particular for $X_N = U_{01}^g$. In the second reformulation we take twice the first double commutator and use the consequence of the diagonality of L_{01}:

$$\varrho\{[H_1, X_N] + [[H_0, U_{01}^g], X_N]\}\varrho = 0 \tag{189}$$

for any nondiagonal X_N, in particular for $X_N = U_{20}^g - U_{20}^{g\dagger} = 2U_{20}^a$.

In the first reformulation we get

$$\begin{aligned}(L_C)_{21} = \frac{1}{2}\varrho\Big\{&[[Y_0^2, H_0]_+, U_{01}^g] \\ &- \frac{1}{2}[[H_0, U_{01}^g], Y_0^2]_+ \\ &+ \frac{1}{2}[[H_0, Y_0^2], U_{01}^g]_+ \\ &- [H_0, [Y_0^2, U_{01}^g]]_+ + 2[H_1, U_{20}^a] \\ &- [H_0, Y_{01}Y_0 + Y_0 Y_{01}]_+ \\ &- [H_1, Y_0^2]_+ + 2Y_{01} V Y_0 + 2Y_0 V Y_{01}\Big\}. \end{aligned} \tag{190}$$

The sum of all contributions involving H_0, Y_0^2, and U_{01}^g is

$$\frac{1}{2}\varrho[H_0, [U_{01}^g, Y_0^2]_+]\varrho = 0, \tag{191}$$

which vanishes by virtue of the Brillouin condition for H_0 ($[U_{01}^g, Y_0^2]_+$ is an anti-Hermitian operator). So the final result is

$$\begin{aligned}(L_C)_{21} = \varrho\Big\{&U_{20}^{g\dagger} H_1 + H_1 U_{20}^g \\ &- \frac{1}{2}[Y_{01}Y_0 + Y_0 Y_{01}, H_0]_+ \\ &+ Y_{01} V Y_0 + Y_0 V Y_{01}\Big\}\varrho. \end{aligned} \tag{192}$$

The matrix elements of L_{21} in the model space are

$$\begin{aligned}
&\langle \varphi_i^{(0)}|L_{21}|\varphi_j^{(0)}\rangle \\
&\quad = \langle \varphi_i^{(2,0)}|H_1|\varphi_j^{(0)}\rangle + \langle \varphi_i^{(0)}|H_1|\varphi_j^{(2,0)}\rangle \\
&\qquad + \langle \varphi_i^{(0)}|Y_{01}\left[V - \frac{1}{2}\left(\varepsilon_i^{(0)} + \varepsilon_j^{(0)}\right)\right]Y_0|\varphi_j^{(0)}\rangle \\
&\qquad + \langle \varphi_i^{(0)}|Y_0\left[V - \frac{1}{2}\left(\varepsilon_i^{(0)} + \varepsilon_j^{(0)}\right)\right]Y_{01}|\varphi_j^{(0)}\rangle \\
&\quad = \langle \varphi_i^{(2,0)}|\vec{\sigma}\vec{A}|\chi_j^{(0)}\rangle + \langle \chi_i^{(2,0)}|\vec{\sigma}\vec{A}|\varphi_j^{(0)}\rangle \\
&\qquad + \langle \chi_i^{(0)}|\vec{\sigma}\vec{A}|\varphi_j^{(2,0)}\rangle + \langle \varphi_i^{(0)}|\vec{\sigma}\vec{A}|\chi_j^{(2,0)}\rangle .
\end{aligned} \tag{193}$$

In the second reformulation we get

$$\begin{aligned}
(L_C)_{21} = \frac{1}{2}\varrho\Big\{ &-\frac{1}{2}\left[\left[H_0, U_{01}^g\right], Y_0^2\right]_+ \\
&+\frac{1}{2}\left[\left[H_0, Y_0^2\right], U_{01}^g\right]_+ \\
&-\left[\left[Y_0^2, U_{01}^g\right], H_0\right]_+ \\
&-\left[Y_{01}Y_0 + Y_0Y_{01}, H_0\right]_+ \\
&-\left[Y_0^2, H_1\right]_+ + 2\left[Y_0VY_0, U_{01}^g\right] \\
&+2Y_{01}VY_0 + 2Y_0VY_{01}\Big\}\varrho .
\end{aligned} \tag{194}$$

We further insert

$$H_1 = L_{01} - \left[H_0, U_{01}^g\right]. \tag{195}$$

The sum of all contributions involving H_0, Y_0^2, and U_{01}^g is now

$$\begin{aligned}
&\frac{3}{2}H_0U_{01}^gY_0^2 - \frac{3}{2}Y_0^2U_{01}^gH_0 - \frac{1}{2}H_0Y_0^2U_{01}^g \\
&\quad + \frac{1}{2}U_{01}^gY_0^2H_0 \\
&\quad = H_0U_{01}^gY_0^2 + Y_0^2U_{01}^{g\dagger}H_0 + \frac{1}{2}\left[H_0, \left[U_{01}^g, Y_0^2\right]_+\right].
\end{aligned} \tag{196}$$

We finally get, using (191),

$$\begin{aligned}
(L_C)_{21} = \varrho\Big\{ &U_{01}^{g\dagger}Y_0VY_0 + Y_0VY_0U_{01}^g - \frac{1}{2}\left[Y_0^2, L_{01}\right]_+ \\
&-Y_0^2U_{01}^gH_0 - H_0U_{01}^{g\dagger}Y_0^2 \\
&-\frac{1}{2}\left[Y_{01}Y_0 + Y_0Y_{01}, H_0\right]_+ \\
&+Y_{01}VY_0 + Y_0VY_{01}\Big\}\varrho ,
\end{aligned} \tag{197}$$

$$\begin{aligned}
&\langle \varphi_i^{(0)}|L_{21}|\varphi_j^{(0)}\rangle \\
&\quad = \langle \varphi_i^{(0,1)}|Y_0\left[V - \frac{1}{2}\left(\varepsilon_i^{(0)} + \varepsilon_j^{(0)}\right)\right]Y_0|\varphi_j^{(0)}\rangle \\
&\qquad + \langle \varphi_i^{(0)}|Y_0\left[V - \frac{1}{2}\left(\varepsilon_i^{(0)} + \varepsilon_j^{(0)}\right)\right]Y_0|\varphi_j^{(0,1)}\rangle \\
&\qquad + \langle \varphi_i^{(0)}|Y_{01}\left[V - \frac{1}{2}\left(\varepsilon_i^{(0)} + \varepsilon_j^{(0)}\right)\right]Y_0|\varphi_j^{(0)}\rangle \\
&\qquad + \langle \varphi_i^{(0)}|Y_0\left[V - \frac{1}{2}\left(\varepsilon_i^{(0)} + \varepsilon_j^{(0)}\right)\right]Y_{01}|\varphi_j^{(0)}\rangle \\
&\qquad - \frac{1}{2}\sum_l \langle \chi_i^{(0)}|\chi_l^{(0)}\rangle\langle \varphi_l^{(0)}|L_{01}|\varphi_j^{(0)}\rangle \\
&\qquad - \frac{1}{2}\sum_l \langle \varphi_i^{(0)}|L_{01}|\varphi_l^{(0)}\rangle\langle \chi_l^{(0)}|\chi_j^{(0)}\rangle \\
&\quad = \langle \chi_i^{(0)}|V - \frac{1}{2}\left(\varepsilon_i^{(0)} + \varepsilon_j^{(0)}\right)|\chi_j^{(0,1)}\rangle \\
&\qquad + \langle \chi_i^{(0,1)}|V - \frac{1}{2}\left(\varepsilon_i^{(0)} + \varepsilon_j^{(0)}\right)|\chi_j^{(0)}\rangle \\
&\qquad - \frac{1}{2}\sum_k \langle \chi_i^{(0)}|\chi_k^{(0)}\rangle\langle \varphi_k^{(0)}|L_{01}|\varphi_j^{(0)}\rangle \\
&\qquad - \frac{1}{2}\sum_k \langle \varphi_i^{(0)}|L_{01}|\varphi_k^{(0)}\rangle\langle \chi_k^{(0)}|\chi_j^{(0)}\rangle .
\end{aligned} \tag{198}$$

For $(\tilde{U}\tilde{D}\tilde{U})_{22}$ we obtain a rather lengthy expression:

$$\begin{aligned}
(\tilde{U}\tilde{D}\tilde{U})_{22} = \frac{1}{2}\Big\{ &\left[H_0, U_{22}^g - U_{22}^{g\dagger}\right] + U_{20}^{g\dagger}\left[H_0, U_{02}^g\right] \\
&+\left[U_{20}^{g\dagger}, H_0\right]U_{02}^g + U_{02}^{g\dagger}\left[H_0, U_{20}^g\right] \\
&+\left[U_{02}^{g\dagger}, H_0\right]U_{20}^g + U_{21}^{g\dagger}\left[H_0, U_{01}^g\right] \\
&+\left[U_{21}^{g\dagger}, H_0\right]U_{01}^g + U_{01}^{g\dagger}\left[H_0, U_{21}^g\right] \\
&+\left[U_{01}^{g\dagger}, H_0\right]U_{21}^g\Big\} - \frac{1}{2}\Big[U_{02}^{g\dagger}Y_0^2 \\
&+Y_0^2U_{02}^g + U_{01}^{g\dagger}Y_0^2U_{01}^g + U_{01}^{g\dagger}Y_{01}Y_0 \\
&+U_{01}^{g\dagger}Y_0Y_{01} + Y_0Y_{01}U_{01}^g \\
&+Y_{01}Y_0U_{01}^g + Y_{01}Y_{01}, H_0\Big]_+ \\
&-\frac{1}{2}\Big[U_{01}^{g\dagger}Y_0^2 + Y_0^2U_{01}^g + Y_{01}Y_0
\end{aligned}$$

$$+ Y_0 Y_{01}, H_1\big]_+ - \frac{1}{2}\big[Y_0^2, H_2\big]_+ + U_{02}^{g\dagger} Y_0 V Y_0 + Y_0 V Y_0 U_{02}^g + U_{01}^{g\dagger} Y_{01} V Y_0 + U_{01}^{g\dagger} Y_0 V Y_{01} + Y_{01} V Y_0 U_{01}^g + Y_0 V Y_{01} U_{01}^g + U_{01}^g Y_0 V Y_0 U_{01}^g + Y_{01} V Y_{01}. \quad (199)$$

Of course, U_{22}^g does not contribute to L_{22}. After some manipulations one gets an expression that only contains U_{20}^g and U_{01}^g:

$$\begin{aligned}(L_C)_{22} = {} & U_{20}^{g\dagger} H_2 + H_2 U_{20}^g + U_{20}^{g\dagger} H_1 U_{01}^g + U_{01}^{g\dagger} H_1 U_{20}^g \\ & + (Y_0 V Y_{01} + Y_{01} V Y_0) U_{01}^g \\ & + U_{01}^{g\dagger}(Y_{01} V Y_0 + Y_0 V Y_{01}) \\ & + U_{01}^{g\dagger} Y_0 V Y_0 U_{01}^g + Y_{01} V Y_{01} \\ & - \frac{1}{2}\big[H_0, U_{01}^{g\dagger} Y_0^2 U_{01}^g + U_{01}^{g\dagger}[Y_0, Y_{01}]_+ \\ & + [Y_{01}, Y_0]_+ U_{01}^g + Y_{01}^2\big]_+ \\ & - \frac{1}{2}\big[L_{01}, U_{20}^{g\dagger} U_{01}^g + U_{01}^{g\dagger} U_{20}^g + U_{01}^{g\dagger} Y_0^2 \\ & + Y_0^2 U_{01}^g + Y_0 Y_{01} + Y_{01} Y_0\big]_+ \\ & - \frac{1}{2}\big[L_{20}, U_{01}^{g\dagger} U_{01}^g\big]_+, \end{aligned} \quad (200)$$

which has the matrix elements

$$\begin{aligned}&\langle \varphi_i^{(0)} | L_{22} | \varphi_j^{(0)} \rangle \\ &\quad = \langle \varphi_i^{(2,0)} | \vec{\sigma}\vec{A} | \chi_j^{(0,1)} \rangle + \langle \chi_i^{(0,1)} | \vec{\sigma}\vec{A} | \varphi_j^{(2,0)} \rangle \\ &\qquad + \langle \chi_i^{(2,0)} | \vec{\sigma}\vec{A} | \varphi_j^{(0,1)} \rangle + \langle \varphi_i^{(0,1)} | \vec{\sigma}\vec{A} | \chi_j^{(2,0)} \rangle \\ &\qquad - \frac{1}{2}\sum_k \langle \varphi_i^{(0)} | L_{01} | \varphi_k^{(0)} \rangle \big\{ \langle \varphi_k^{(2,0)} | \varphi_j^{(0,1)} \rangle \\ &\quad + \langle \varphi_k^{(0,1)} | \varphi_j^{(2,0)} \rangle + \langle \chi_k^{(0,1)} | \chi_j^{(0)} \rangle \\ &\quad + \langle \chi_k^{(0)} | \chi_j^{(0,1)} \rangle \big\} - \frac{1}{2}\sum_k \{ \langle \varphi_i^{(2,0)} | \varphi_k^{(0,1)} \rangle \\ &\quad + \langle \varphi_i^{(0,1)} | \varphi_k^{(2,0)} \rangle + \langle \chi_i^{(0,1)} | \chi_k^{(0)} \rangle \\ &\quad + \langle \chi_i^{(0)} | \chi_k^{(0,1)} \rangle \} \langle \varphi_k^{(0)} | L_{01} | \varphi_j^{(0)} \rangle \\ &\qquad + \langle \chi_i^{(0,1)} | V - \frac{1}{2}\big(\varepsilon_i^{(0)} + \varepsilon_j^{(0)}\big) | \chi_j^{(0,1)} \rangle \\ &\qquad - \frac{1}{2}\sum_k \langle \varphi_i^{(0)} | L_{20} | \varphi_k^{(0)} \rangle \langle \varphi_k^{(0,1)} | \varphi_j^{(0,1)} \rangle \\ &\qquad - \frac{1}{2}\sum_k \langle \varphi_i^{(0,1)} \mid \varphi_k^{(0,1)} \rangle \langle \varphi_k^{(0)} | L_2 | \varphi_j^{(0)} \rangle. \end{aligned} \quad (201)$$

The original expression for L_{211} is so lengthy that we merely give the reformulation, which only contains U_{210}, U_{200}, and U_{010}:

$$\begin{aligned}(L_C)_{211} = {} & U_{210}^{g\dagger} H_{001} + H_{001} U_{210}^g + U_{200}^{g\dagger} H_{011} + H_{011} U_{200}^g \\ & + U_{200}^{g\dagger} H_{001} U_{010}^g + U_{010}^{g\dagger} H_{001} U_{200}^g \\ & + U_{010}^{g\dagger}(Y_{001} V Y_0 + Y_0 V Y_{001}) \\ & + (Y_{001} V Y_0 + Y_0 V Y_{001}) U_{010}^g \\ & + Y_{010} V Y_{001} + Y_{001} V Y_{010} \\ & - \frac{1}{2}\big[H_0, U_{010}^{g\dagger}(Y_{001} Y_0 + Y_0 Y_{001}) \\ & + (Y_{001} Y_0 + Y_0 Y_{001}) U_{010}^g \\ & + Y_{010} Y_{001} + Y_{001} Y_{010}\big] \\ & + - \frac{1}{2}[L_{010}, Y_0 Y_{001} + Y_{001} Y_0]_+ \end{aligned} \quad (202)$$

One notes that

$$\vec{\sigma}\vec{A}_2 Y_{200} = Y_{001} V Y_0 - Y_{001} Y_0 H_0, \quad (203)$$

$$\vec{\sigma}\vec{A}_2 Y_{210} = Y_{001} V Y_{010} - Y_{001} Y_{010} H_0 - Y_{001} Y_0 H_{010}. \quad (204)$$

The matrix elements of L_{211} in the active space are

$$\begin{aligned}&\langle \varphi_i^{(0)} | L_{211} | \varphi_j^{(0)} \rangle \\ &\quad = \langle \varphi_i^{(2,1,0)} | \vec{\sigma}\vec{A}_2 | \chi_i^{(0)} \rangle + \langle \chi_i^{(0)} | \vec{\sigma}\vec{A}_2 | \varphi_j^{(2,1,0)} \rangle \\ &\qquad + \langle \varphi_i^{(0)} | \vec{\sigma}\vec{A}_2 | \chi_j^{(2,1,0)} \rangle + \langle \chi_i^{(2,1,0)} | \vec{\sigma}\vec{A}_2 | \varphi_j^{(0)} \rangle \\ &\qquad + \langle \varphi_i^{(2,0,0)} | \vec{\sigma}\vec{A}_2 | \chi_j^{(0,1,0)} \rangle \\ &\qquad + \langle \chi_i^{(0,1,0)} | \vec{\sigma}\vec{A}_2 | \varphi_j^{(2,0,0)} \rangle \\ &\qquad + \langle \chi_i^{(2,0,0)} | \vec{\sigma}\vec{A}_2 | \varphi_j^{(0,1,0)} \rangle \\ &\qquad + \langle \varphi_i^{(0,1,0)} | \vec{\sigma}\vec{A}_2 | \chi_j^{(2,0,0)} \rangle. \end{aligned} \quad (205)$$

FW HAMILTONIAN

There is a simple way from the effective Hamiltonian approach to the FW transformed Hamiltonian.[8] It is sufficient to extend the model space to that of all electronic (positive-energy) wave functions. This means that nondiagonal operators vanish automatically and diagonal operators are replaced by the entire operators. Practically, this means that U^g is replaced to all orders by 1. The

transformed Hamiltonian becomes

$$L = H - \frac{1}{2}c^{-2}[\tilde{Y}^\dagger\tilde{Y}, H]_+ + c^{-2}\tilde{Y}^\dagger V\tilde{Y} - 2m\left(\tilde{Y} - Y_0 - \lambda Y_{01}\right)^\dagger\left(\tilde{Y} - Y_0 - \lambda Y_{01}\right); \quad (206)$$

the leading terms in an expansion in powers of c^{-2} and λ are (we now write H_{pq} rather than L_{pq})

$$H_{00} = H_0, \quad (207)$$

$$H_{01} = H_1 = \frac{1}{2m}[\vec{\sigma}\vec{A}, \vec{\sigma}\vec{p}]_+, \quad (208)$$

$$H_{02} = H_2 = \frac{1}{2m}\vec{A}^2, \quad (209)$$

$$H_{20} = Y_0 V Y_0 - \frac{1}{2}\left[H_0, Y_0^2\right]_+, \quad (210)$$

$$H_{21} = -\frac{1}{2}[Y_{01}Y_0 + Y_0Y_{01}, H_0]_+ - \frac{1}{2}\left[Y_0^2, H_1\right]_+ + Y_{01}VY_0 + Y_0VY_{01}, \quad (211)$$

$$H_{22} = -\frac{1}{2}\left[Y_{01}^2, H_0\right]_+ - \frac{1}{2}[Y_{01}Y_0 + Y_0Y_{01}, H_1]_+ - \frac{1}{2}\left[Y_0^2, H_2\right]_+ + Y_{01}VY_{01}, \quad (212)$$

$$H_{011} = \frac{1}{2m}[\vec{\sigma}\vec{A}_1, \vec{\sigma}\vec{A}_2]_+, \quad (213)$$

$$H_{211} = -\frac{1}{2}[Y_{001}Y_{010} + Y_{010}Y_{001}, H_0]_+ - \frac{1}{2}[[Y_{001}, Y_0]_+, H_{010}]_+ - \frac{1}{2}[[Y_{010}, Y_0]_+, H_{001}]_+ - \frac{1}{2}\left[(Y_0)^2, H_{011}\right]_+ + Y_{001}VY_{010} + Y_{010}VY_{001}, \quad (214)$$

with

$$Y_0 = \frac{1}{2m}\vec{\sigma}\vec{p}, \quad Y_{01} = \frac{1}{2m}\vec{\sigma}\vec{A}; \quad (215)$$

$$Y_{010} = \frac{1}{2m}\vec{\sigma}\vec{A}_1; \quad Y_{001} = \frac{1}{2m}\vec{\sigma}\vec{A}_2. \quad (216)$$

If one cares for expressions for magnetic properties and their relativistic corrections, one must perform perturbation theory with the FW Hamiltonian. However, this is possible to only a limited extent. In those cases where this is possible, one gets exactly the result derived in previous sections of this article and one need not repeat this.

If one wants, one can decompose the contributions to the FW Hamiltonian into scalar and spin-dependent terms.

Conclusions

DPT is a straightforward method to evaluate relativistic corrections to the energy, as well as to any kind of properties in terms of regular expressions. This would not be possible starting from FW transformation, which yields regular results only to the leading order in c^{-2}.

Because relativity and an external magnetic field both lead to a splitting of the one-electron levels, it is preferable to generalize the multiple perturbation formalism for a single state to that for a set of degenerate states, which will be split by the perturbation. This was done.

Here we only considered one-electron Hamiltonians. In order to generalize this formalism to the many-electron case, an important first step is to formulate double (or triple) perturbation theory in the context of a coupled-Hartree–Fock or coupled multi-configuration–self-consistent field approach. This will be done in a subsequent article,[17] based upon the quasidegenerate formalism outlined here. In this formalism one may or may not include the Breit interaction.

In one-electron systems, as studied in this article, the choice of the gauge is not very critical. Usually one will be able to find an optimum local gauge. In many-electron systems, however, the gauge problem needs special attention and has to be treated as in the IGLO or GIAO approaches.[31–36]

Acknowledgments

The author thanks M. Dahlbeck, R. Franke, W. Klopper, and Ch. van Wüllen for valuable comments.

References

1. Sewell, G. L. Proc Cambridge Phil Soc 1949, 45, 631.
2. Rutkowski, A. J Phys B 1986, 19, 149, 3419, 3434.
3. (a) Kutzelnigg, W. Z Phys D 1989, 11, 15; (b) Kutzelnigg, W. Z Phys D 1990, 15, 27.

4. This can even be traced back to W. Pauli's article: In Handbuch Physik; Geiger, H.; Scheel, K.; eds.; Springer: Berlin, 1933; Vol. 24/1, p. 237, reprinted practically unchanged In Handbuch Physik; Flügge, S., ed.; Springer: Berlin, 1958; Vol. V/1.
5. (a) Gesteszy, F.; Grosse, H.; Thaller, B. Phys Lett 1982, 116B 155; (b) Gesteszy, F.; Grosse, H.; Thaller, B. Phys Rev D 1984, 30, 2189.
6. Thaller, B. The Dirac Equation; Springer: Berlin, 1992.
7. Kutzelnigg, W. Chem Phys 1997, 225, 203.
8. Kutzelnigg, W. J Chem Phys 1999, 110, 8283.
9. Nomura, Y.; Takeuchi, Y.; Nakagawa, N. Tetrahedron Lett 1969, 8, 639.
10. Nakatsuji, H.; Takashima, H.; Hada, M. Chem Phys Lett 1995, 233, 95.
11. (a) Fukui, H.; Baba, T.; Imonata, H. J Chem Phys 1996; 105, 3175; (b) Fukui, H.; Baba, T.; Imonata, H. J Chem Phys 1997, 106, 2987.
12. Kutzelnigg, W. Theor Chim Acta 1988, 73, 173.
13. Ballard, C. C.; Hada, M.; Kaneko, H.; Nakatsuji, H. Chem Phys Lett 1996, 254, 170.
14. Kaupp, M.; Malkin, V. G.; Malkina, O. L. In Encyclopedia of Computational Chemistry; Schleyer, P. v. R.; Allinger, N. L.; Clark, T.; Gasteiger, J.; Kollman, P. A.; Schaefer III, H. F.; Schreiner, P. R., Eds.; Wiley: Chichester, U. K., 1998.
15. Kutzelnigg, W. Phys Rev A 1996, 59, 1183.
16. Kutzelnigg, W.; Liu, W., unpublished.
17. Kutzelnigg, W.; Dahlbeck, M.; van Wüllen, C.; Franke, R., unpublished.
18. Pyykkö, P. Chem Phys 1977, 22, 289.
19. Pyykkö, P. Chem Phys 1983, 74, 1.
20. (a) Ramsey, N. F. Phys Rev 1950, 77, 567; (b) Ramsey, N. F. Phys Rev 1950, 78, 699; (c) Ramsey, N. F. 1951, 83, 540; (d) Ramsey, N. F. Phys Rev 1952, 86, 243.
21. Visscher, L.; Enevoldsen, T.; Saue, T.; Jensen, H. J. A.; Oddershedde, J. J Comput Chem to appear.
22. Dalgarno, A.; Stewart, A. L. Proc Roy Soc 1956, 238, 269, 276.
23. Lévy–Leblond, J. M. Commun Math Phys 1967, 6, 286.
24. Franke, R.; Kutzelnigg, W. Chem Phys Lett 1992, 199, 561.
25. Ottschofski, E.; Kutzelnigg, W. J Chem Phys 1995, 102, 1752.
26. Heully, J. C.; Lindgren, I.; Lindroth, E.; Lundquist, S.; Mårtenson–Pendrill, A. M. J Phys B 1986, 19, 2799.
27. Rutkowski, A.; Schwarz, W. H. E. J Chem Phys 1996, 104, 8546.
28. Rutkowski, A.; Schwarz, W. H. E.; Kozłowski, R.; Bęczek, J.; Franke, R. J Chem Phys 1998, 109, 2135.
29. Kutzelnigg, W. J Chem Phys 1982, 77, 3081.
30. Kutzelnigg, W.; Koch, S. J Chem Phys 1983, 79, 4315.
31. Kutzelnigg, W. Israel J Chem 1980, 19, 193.
32. Schindler, M.; Kutzelnigg, W. J Chem Phys 1982, 76, 1919.
33. London, F. J Phys Radium 1937, 8, 397.
34. Ditchfield, R. J Chem Phys 1972, 56, 5688.
35. Häser, M.; Ahlrichs, R.; Baron, A. P.; Weiss, P.; Horn, C. Theor Chim Acta 1992, 83, 435.
36. Wolinsky, K.; Honton, J. F.; Pulay, P. J Am Chem Soc 1990, 112, 8251.